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(54) **Method for improving wear resistance of polymeric bio-implantable components**

Verfahren zur Verbesserung der Verschleissfestigkeit von biokompatiblen Polymerkomponenten

Procédé d'amélioration de la résistance à l'usure de composants polymériques biocompatibles

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- **INTERNATIONAL JOURNAL OF RADIATION/APPLICATIONS & INSTRUMENTATION PART C, vol. 31, no. 4-6, 1988, GB, pages 693-698, XP002009662 R.M. STREICHER: "INFLUENCE OF IONIZING IRRADIATION IN AIR AND NITROGEN FOR STERILIZATION OF SURGICAL GRADE POLYETHYLENE FOR IMPLANTS."**

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Description

[0001] This invention relates to bioimplantable polymeric articles and more particularly to methods of improving the wear resistance and oxidation resistance of such articles.

[0002] Advances in biomedical engineering have resulted in numerous polymeric articles which are able to be implanted within the body. Polymeric components are widely used in orthopedic surgery, for example, to form articulation surfaces within artificial joints. Ultrahigh molecular weight polyethylene (UHMWPE) is an example of a polymer that is commonly used to form components of artificial joints.

[0003] Among the properties required of bioimplantable polymeric components, particularly those used in artificial joints, are low friction, biocompatibility, and good mechanical properties, including excellent resistance to wear. Such components must also be sterile before implantation within a patient.

[0004] Some polymers and medical devices may be adversely affected by heat sterilization, thus such a technique is not widely used. Ethylene oxide sterilization is another technique for sterilizing medical devices, but ethylene oxide can pose health and environmental risks that render this method less desirable. As a result, a preferred method of sterilizing many medical devices, including polymeric components, is by exposure to forms of ionizing radiation such as gamma rays, x-rays, or electron beam radiation.

[0005] Presently, sterilization by gamma radiation is a preferred method for sterilizing many medical devices, including bioimplantable polymeric components. One potential effect of gamma radiation sterilization is that the gamma rays can initiate chemical reactions within the polymer that can affect the structure, morphology and some mechanical properties of the polymer. During gamma irradiation a variety of chemical species, such as ions, excited molecules, double bonds, oxidation products and free radicals are created within the polymer. Free radicals are believed to be a species generated during gamma radiation that may contribute most to changes in the properties of irradiated polymers.

[0006] Once free radicals are formed within a polymer, these species may participate in at least four types of major reactions. The free radicals can undergo a recombination reaction by reacting with hydrogen to eliminate the free radical, by reacting with carbon molecules to create side chains, or both. Free radicals can also undergo a chain scission reaction that results in a decrease in the molecular weight of the polymer, and an increase in the density and crystallinity of the polymer, thus causing some mechanical properties of the polymer to degrade. A crosslinking reaction is another reaction in which the free radicals can participate. Finally, the free radicals may remain within a polymeric material without reacting initially, thus remaining available to react over time as conditions dictate.

[0007] The presence of oxygen in polymeric materials and their surrounding environment can contribute to an oxidation reaction in which free radicals and dissolved oxygen react to produce a compound with a carbonyl functional group, resulting in chain scission and the creation of new free radicals. Oxidation can decrease the molecular weight of a polymer (due to chain scission) and contribute to the degradation of its mechanical properties.

[0008] Sterilization of polymer components by gamma radiation in air is believed to decrease the wear resistance of polymers due, in part, to oxidation effects. Wear resistance is a key mechanical property for polymeric components that are used in joint prostheses. As a result, a current practice is to sterilize polymeric components in an environment of an inert gas (e.g., argon, helium, nitrogen) to minimize oxidation effects. *See,* Kurth, M. et al., *"Effects of Radiation Sterilization on UHMW-Polyethylene"* Antec 87, pp. 1193-1197 (1987); Streicher, RK., *Radiol. Phys. Chem.,* Vol. 31, Nos. 4-6, pp. 693-698 (1988); Streicher, R.M., "Improving UHMWPE by Ionizing Radiation Crosslinking During Sterilization", 17th Annual Meeting of the Society for BioMaterials, p. 181 (1991). Others have used vacuum techniques to help purge an environment of oxygen before conducting gamma radiation sterilization. *See,* Yong Zhao, et al., *J. Appl. Polymer Sci.,* Vol. 50, pp. 1797-1801 (1993).

[0009] Wear resistance is a property of great importance to artificial joint components. Natural friction within a replaced, artificial joint can cause minute particles of debris (e.g., particles from a polymeric component) to become dislodged and to migrate within the joint. This phenomenon of wear debris within artificial joints is a serious problem that can inhibit the proper mechanical functioning of the joint. Wear debris can also lead to osteolysis and bone deterioration. If osteolysis develops around an artificial joint it is usually corrected by surgical removal of the diseased tissue and revision of the artificial joint. WO-A-9 427 651 discloses a method of producing an orthopedic device, packing the device in an airtight container, subjecting the container to vacuum, sealing the container, applying atmospheric pressure and subjecting the container to irradiation.

[0010] Because excellent wear resistance is a property of such importance for polymeric components used to form artificial joints, it would be advantageous to be able to provide sterilized polymer components that have improved wear resistance.

[0011] It is thus an object of the invention to provide methods for increasing the wear resistance of bioimplantable polymeric components.

SUMMARY OF THE INVENTION

[0012] The invention, as defined in claims 1, 11 and 12, provides methods for increasing the wear resistance of a polymeric manufactured part. Each method is particularly well suited to polymeric parts that are biocompatible and that are intended for use as components of artificial joints. A variety of polymeric materials, particularly UHMWPE, can be treated according to the invention to improve wear resistance and to improve oxidation resistance.

[0013] According to the method of the invention as defined in claim 1, one or more manufactured polymeric parts, such as a bioimplantable component, are placed within one or more gas impermeable, flexible packages. Each package has at least one heat sealable opening therein. The packages and the parts therein are then subjected to a relatively strong vacuum force. While under the influence of the vacuum, the packages are heat sealed and after sealing, hydrostatic pressure is exerted on the part. Typically, the package is heat sealed shortly after initiating the vacuum, and usually not more than one-half hour after initiating the vacuum. Next, the packages and the parts that are contained within the packages are irradiated for a period of time that is sufficient to sterilize the parts and to promote crosslinking of the polymer that forms the part. Various forms of ionizing energy can be used to sterilize the parts. However, the use of gamma radiation is among the more preferred radiation sterilization techniques.

[0014] In another embodiment, manufactured polymeric parts can be placed within a packaging container that is either flexible or rigid. After minimizing or eliminating the oxygen concentration within the container, the container is pressurized to 1.5 to 4 atmospheres with an inert gas, or with a mixture of an inert gas and hydrogen. Thereafter, the parts and the containers are irradiated for a period of time sufficient to sterilize the parts and to promote crosslinking of the polymer that forms the part.

[0015] This process has been found to increase the wear resistance of polymeric parts while maintaining other mechanical properties that are important to such parts. An additional benefit of the invention is the improved ability of the polymeric parts to resist oxidation. The resulting sterilized part is characterized by a gel content in the range of 75 to 100%, indicating high levels of crosslinking within the polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 is a bar graph which plots wear rate (milligrams of weight lost per 1 million cycles) for various samples evaluated in Example 3.

[0017] Figure 2 is a bar graph which plots wear rate (mm^3 of wear per 1 million cycles) for various samples evaluated in Example 4.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Many polymeric components, such as those comprising UHMWPE, form articulation surfaces for artificial joints. Thus, it is essential that these components possess excellent wear resistance.

[0019] The present invention provides a method for improving the wear resistance of manufactured polymeric parts. According to this process the desired polymeric part is first manufactured by known processes, such as compression molding and RAM extrusion. The polymer that forms the part can be low density polyethylene, high density polyethylene, ultrahigh molecular weight polyethylene, polypropylene, polyester, nylon, polyurethane, poly(methylmethacrylate), or other biocompatible polymers typically used in biomedical applications. A preferred polymer is UHMWPE, which is commonly used in a variety of orthopedic implants, such as liners for acetabular shells of artificial hip joints, and as tibial bearing members in artificial knee joints.

[0020] In one embodiment, polymeric parts that are to be subjected to the process of the invention are first placed in a flexible package that has a heat sealable opening therein. Preferably, each part is individually packaged, but more than one part can be placed in a single package. The package and the part are then subjected to a relatively high vacuum force while the heat sealable opening remains open. The vacuum force is maintained for 10 seconds to 30 minutes, and preferably for about 30 seconds. Thereafter, the package is heat sealed, while maintaining the vacuum force, rendering the package gas impermeable. Once the package is sealed under vacuum, and following removal of the vacuum force, a hydrostatic guage pressure in the range of 48 to 101 KN/m^2 (7 to 14.7 psig) is exerted on the part.

[0021] The packaging of the polymeric parts in a heat sealed package under vacuum is effective to reduce pressure within the package and to remove oxygen from the polymeric material and from the environment within the package. Moreover, the hydrostatic pressure which is exerted on the polymeric part is believed to hinder the evolution of hydrogen gas from within the polymer during irradiation.

[0022] Following the vacuum heat sealing of the package that contains the polymeric part, the package and the part are irradiated for a period of time that is sufficient to sterilize the part and to initiate crosslinking of polymer chains within the manufactured part. Various acceptable forms of ionizing radiation can be used to effect the sterilization of the part. These radiation forms include gamma rays, x-rays, and electron beam radiation. Currently, the use of gamma

radiation is a preferred irradiation technique.

[0023] In one aspect of the invention the concentration of hydrogen within the package is in the range of 30 to 100% by volume. Preferably, the polymeric part is aged in the hydrogen rich gas within the packaging container for a period of time sufficient to enable hydrogen atoms to recombine with any free radicals present within the polymeric parts. Preferably, a suitable aging period is at least 48 hours following irradiation of the part and the packaging container.

[0024] The flexible packaging material within which the polymeric parts are sealed can be selected from among many types of high barrier, flexible packaging material that are commonly used to enclose medical devices. Preferably the packaging material is a multilayered, heat seal peelable packaging material that includes one or more foil layers, various polymer layers and a heat seal coating. Examples of suitable materials are those that include the following layers: polyester film-low density polyethylene-foil-ionomer-heat seal coating. Packaging materials having the following layers can also be used: polyester-low density polyethylene-foil-EAA-linear low density polyethylene-heat seal coating; and polyester-Surlyn-nylon-Surlyn-foil-EAA-linear low density polyethylene-heat seal coating. Suitable packaging materials can be obtained from a variety of sources, including Tolas Health Care Packaging of Feasterville, Pennsylvania. The thickness of the packaging material preferably is in the range of 0.05 to 1.8 mm (2 mil to 7 mil).

[0025] According to the process of the invention, a relatively strong vacuum force is used which is sufficient to remove all or substantially all oxygen from within the package and the adjacent environment. The vacuum force utilized is in the range of 500 to 1013 mbar. A preferred vacuum force is approximately 1000 mbar. Typically, the vacuum force is exerted upon the package and the polymeric material for 10 seconds to 30 minutes, and preferably for about 30 seconds. While the vacuum force is maintained, the package is heat sealed, rendering it impermeable to gases. Techniques for heat sealing such packaging material while under vacuum force are readily available to those of ordinary skill in the art. Suitable vacuum packaging equipment that is capable of heat sealing packages under vacuum will be known to those of ordinary skill in the art. An example of a suitable vacuum packaging apparatus is a MultiVac A342 apparatus, available from Multivac, Inc. of Kansas City, Missouri.

[0026] As noted above, the packaged polymeric material preferably is irradiated using gamma radiation. The gamma radiation is administered for a duration and at a dose level which is known to be acceptable for sterilizing medical devices. A dose of 20-60 KGy usually is acceptable, while 35 to 50 KGy is preferred. The irradiation step typically continues for approximately 10 minutes up to about several hours and most preferably for one to three hours.

[0027] In another embodiment, manufactured polymeric parts can be placed in either a rigid or a flexible container. Substantially all of the oxygen within the container is first evacuated. Next, the container is pressurized with an inert gas (e.g. argon, helium or nitrogen), or with a mixture of an inert gas and hydrogen, to 1.5 to 4 atmospheres. Subsequently, the container and the enclosed polymeric parts are irradiated (using gamma, x-ray, or electron beam radiation) to an extent sufficient to sterilize the parts and to promote crosslinking of the polymer that forms the parts.

[0028] A variation of this embodiment can also be utilized by dispensing of the need to evacuate the container. According to this variation, the container is first flushed with a sufficient amount of an inert gas to displace any oxygen, and then the container is pressurized to the desired level with an inert gas, or with a mixture of an inert gas and hydrogen.

[0029] A pressurizing gas that is a mixture of an inert gas and hydrogen preferably is hydrogen enriched. The hydrogen enriched inert gas mixture should have a minimum of 2.2×10^{-3} moles of hydrogen gas per gram of polymeric material within the packaging container. In addition, the hydrogen gas within the volume of the packaging container preferably is in the range of 30% to 95% by volume.

[0030] In this embodiment it may also be useful to age the polymeric part following irradiation, for a period of time sufficient to enable hydrogen atoms to recombine with any free radicals within the polymeric parts. A suitable time period preferably is at least 48 hours.

[0031] One of ordinary skill in the art can readily choose a suitable packaging container suitable to be pressurized to 1.5 to 4 atmospheres with an inert gas. Any flexible container that is utilized must, of course, have seals strong enough to withstand the pressures to which it will be subjected.

[0032] The irradiation of polymers is known to create a variety of chemical species, including free radicals, within the chains of the polymer. Free radicals, as noted above, can participate in a number of reactions. It is believed that the technique of the present invention creates a chemical environment that favors free radicals participating in crosslinking reactions with adjacent polymer chains due to the lack of oxygen available in the system for oxidation reactions. Further, irradiation of the polymer also results in the evolution of hydrogen gas in a quantity that is proportional to the quantity of free radicals created. It is further believed that the use of a technique which packages the polymeric part in a gas impermeable, flexible container, under vacuum, causes hydrostatic pressure to be exerted on the bulk material. The processes of the present invention are believed to be effective to inhibit the diffusion of hydrogen out of the material. In addition, in embodiments where the packaging container is charged to 1.5 to 4.0 atmospheres with an inert gas, the elevated pressure is believed to inhibit hydrogen diffusion. In other embodiments, the use of a flexible packaging container is believed to enable the developed hydrostatic pressure to hinder diffusion of hydrogen out of the material. These phenomena are believed to help reduce the number of free radicals present within the bulk polymer, thus further reducing the potential for oxidation of the material.

[0033] As noted above, the techniques of the present invention are believed to contribute to reducing the amount of hydrogen that diffuses from the bulk polymer, thus maintaining more hydrogen within the polymer. This phenomenon is believed to minimize the extent of chain scission reactions within the polymer since the hydrogen within the polymer evidently decreases the number of free radicals within the polymer available to participate in oxidation reactions by recombining with the free radicals. Following packaging, the concentration of hydrogen within the packaging container is maintained below 2.2 x 10^{-5} moles/gram, and more preferably at about 1.83 x 10^{-5} moles/gram.

[0034] The present invention is also believed to contribute to extensive crosslinking within the polymer. This crosslinking is believed to be responsible for increasing the wear resistance of the polymer since molecular weight is increased and chain scission is less prevalent.

[0035] The following examples serve to further illustrate the invention.

EXAMPLES

Example 1

[0036] Disks having a diameter of 25.4 mm and a thickness of 12.7 mm were machined from compression molded UHMWPE (GUR 412, available from Poly Hi Solidur/Meditech of Vreden, Germany). The disks were then sealed in flexible, polymer coated/aluminum foil packages under the following conditions. One set of samples was exposed to a 1,000 mbar vacuum prior to sealing of the package, another set of samples was packaged and sealed in air at -300 mbar, and a third set of samples was exposed to vacuum force of 1000 mbar then backfilled with nitrogen to a pressure of -300 mbar prior to sealing. After sealing, all samples were gamma irradiated with a dose of 40 KGy for about 2 hours 20 minutes. Hydrogen gas composition within the packages was measured after sterilization. All measurements were conducted at the same temperature (23° C) and the pressure inside the bag was equal after sterilization for all samples, i.e., the stiffness of the packages did not contribute to the final package volume. The data obtained are presented in Table 1.

Table 1:

Hydrogen Gas Measurement			
	Hydrogen Gas (moles/g)		
Sample	Vacuum	Air	Nitrogen
1	1.81 x 10^{-5}	2.35 x 10^{-5}	2.40 x 10^{-5}
2	1.87 x 10^{-5}	2.37 x 10^{-5}	2.39 x 10^{-5}
3	1.94 x 10^{-5}	2.76 x 10^{-5}	2.30 x 10^{-5}
4	1.75 x 10^{-5}	2.40 x 10^{-5}	-
5	1.79 x 10^{-5}	2.29 x 10^{-5}	-
6	-	2.58 x 10^{-5}	-
Avg	1.83 x 10^{-5}	2.46 x 10^{-5}	2.36 x 10^{-5}
Std. Dev.	7.29 x 10^{-7}	1.59 x 10^{-6}	5.38 x 10^{-7}

[0037] The data of Table 1 indicates that a significantly lesser amount of hydrogen was present within the packages of samples that were processed according to the technique of the present invention. Presumably, more hydrogen remains present within the bulk polymer as the hydrostatic pressure exerted on the polymer hinders the diffusion of hydrogen from the polymer.

Example 2

[0038] The gel content of UHMWPE samples was determined according to Method C of ASTM D2765-90 to assess the degree of crosslinking within the polymer. UHMWPE films, 200 microns thick and weighing 0.6 grams, were skived from compression molded GUR 412 UHMWPE. Five films were packaged in air while five films were packaged under a 1000 mbar vacuum in a manner identical to that used in Example 1. After packaging, all the samples were sterilized using gamma radiation at 40 KGy for 2 hours 20 minutes.

[0039] The data illustrated in Table 2 indicate that the samples irradiated in air developed no gel. This implies that the number average molecular weight of these samples was reduced from approximately 3,000,000 to less than

500,000. Conversely, the vacuum packaged samples had an average gel content of 87.98%, indicating that extensive crosslinking had occurred within these samples.

Table 2:

Gel Content		
Sample	Vacuum Packaged	Air Packaged
1	88.75	0
2	88.33	0
3	87.60	0
4	86.98	0
5	88.25	0
Avg	87.98	0

[0040] The wear resistance of UHMWPE components processed according to the present invention was also evaluated as explained in Examples 3 and 4.

Example 3

[0041] Ten hip cup liners were machined from compression molded GUR 412 UHMWPE. Five were packaged under vacuum and five were packaged in air according to the procedure explained in Example 1. Ten other hip cup liners were machined from RAM extruded GUR 415 UHMWPE (available from Poly Hi Solidur of Fort Wayne, Indiana). These samples were tested using a 12-station MATCO/PM-MED hip simulator. This simulator is a computer-controlled hydraulic system that produces a biaxial rocking motion of the cups, which is synchronized with the Paul hip loading curb (Paul, J.P., *Proc. Inst. Mech. Eng.*, 181(3J):8-15, 1966). A body weight of 756 N was used, which results in a maximum applied load of 1966 N. All simulator tests were run at 1.1 Hz for at least two million cycles. At seven selected intervals, polyethylene wear was measured on the basis of sample weight loss. All weight loss values were corrected for sample fluid absorption by measuring the weight gains of several untested samples soaked in serum at identical intervals. Wear rates were determined by linear regression of the wear data, beginning after an initial nonlinear period (about 100,000 cycles). Total wear was determined by subtracting the final weight for each sample from the initial weight (approximately 6 grams) and correcting for weight gain due to fluid absorption as described above.

[0042] Data illustrated in Figure 1 indicate that the samples packaged and irradiated in air lost approximately 30 milligrams of weight during the test period while samples packaged under vacuum lost only about 16 milligrams of weight during the testing period. Similarly, the RAM extruded UHMWPE samples resulted in a greater weight loss for air packaged samples (about 28 mg) than for vacuum packaged samples (about 17 mg).

[0043] The increased weight loss of the air packaged and irradiated samples is indicative of a lower resistance to wear which evidently results from chain scission reactions that take place within the polymer, thus reducing the molecular weight of the polymer.

Example 4

[0044] Wear resistance was also evaluated according to another technique in which erosion of a sample caused by revolution of the sample under a metal pin was evaluated. According to this experiment, ten samples of compression molded UHMWPE (GUR 412) disks were obtained together with ten samples of RAM extruded UHMWPE (GUR 415). All samples had the dimensions of 1.25 inches diameter and 0.25 inch thickness. Five samples of each material type were packaged and irradiated in air while five samples of each material type were packaged and irradiated under vacuum, as specified in Example 1.

[0045] Following packaging and irradiation, each sample was evaluated for wear resistance by a "Pin-on-Disk" technique. According to this technique, a metal pin having a diameter of approximately 0.25 inch was placed in contact with a surface of each of the test samples. The pin was loaded to 152 N while the disk was rotated at 112 rpm. The wear track created by the metal pin was measured at 5 intervals over 2,000,000 cycles using a profilometer to detect volume changes in the UHMWPE sample. A linear regression was performed on the volume changes over the second through the fifth measurements to determine the wear rate.

[0046] As illustrated in Figure 2, the GUR 412 compression molded samples packaged and irradiated in air demonstrated a significantly greater wear rate (1.01 mm^3/1,000,000 cycles) than did the samples that were packaged and

irradiated under vacuum (0.48 mm^3/1,000,000 cycles). The RAM extruded GUR 415 samples demonstrated a less significant reduction in wear rate for the vacuum packaged and irradiated samples. As shown in Figure 2, the air packaged and irradiated samples demonstrated the wear rate of 0.78 mm^3/1,000,000 cycles, while the vacuum packaged and irradiated samples demonstrated a wear rate of 0.74 mm^3/1,000,000 cycles.

[0047] A second wear criterion was also used in conjunction with this evaluation. Pitting of the wear track was qualitatively evaluated to further assess the effects of wear. Table 3 illustrates this data in which pits present within a wear track were observed.

Table 3:

Track Pitting		
	Presence of Pits In Sampled Wear Tracks	
Sample	Air Sterilized	Vacuum Sterilized
GUR 412	3 of 6 samples	0 of 6 samples
GUR 415	2 of 6 samples	0 of 6 samples

Claims

1. A method for improving the wear resistance of a polymeric manufactured part, comprising the steps of

   providing one or more manufactured polymeric parts; placing the parts in one or more gas impermeable, flexible packaging containers

   wherein each container has at least one heat sealable opening therein;
   subjecting the packaging container and the polymeric parts to a vacuum force; heat sealing the flexible packaging container while subjected to the vacuum force and, upon sealing of the packaging container, exerting a hydrostatic pressure on the
   irradiating the heat sealed packages and the parts under the pressure for a period of time sufficient to sterilize the parts and
   following the step of irradiating, ageing the polymeric parts within the atmosphere of the packaging container for a period of time;
   wherein the vacuum force is sufficient to remove substantially all of the oxygen from within the packaging container,
   the vacuum force being in the range of 500-1013 mbar.

2. The method of claim 1, wherein the hydrostatic gauge pressure exerted on the part is in the range of 48 to 101 KN/m^2 (7 to 14.7 psig).

3. The method of claims any one of the preceding, wherein any gas within the flexible packaging container after irradiation has less than 2.2 x 10^{-5} moles/g of hydrogen.

4. The method of any one of claims 1 to 3, wherein, following the step of irradiating, the part is **characterized by** a gel content in the range of 75 to 100% as determined by Method C of ASTM D2765-90.

5. The method of any one of claims 1 to 4, wherein the flexible packaging container is manufactured of a metal foil that is surrounded by one or more layers of a polymer film.

6. The method of any one of claims 1 to 5, wherein the polymeric part is made from a polymer selected from the group consisting of low density polyethylene, high density polyethylene, ultrahigh molecular weight polyethylene, polypropylene, polyester, nylon, polyurethane, and poly(methylmethacrylate).

7. The method of any one of claims 1 to 6, wherein the polymeric part is made from an ultrahigh molecular weight polyethylene having a number average molecular weight greater than 1.0 million.

8. The method of claim 6 or claim 7, wherein the polymeric part is manufactured by a compression molding process.

9. The method of claim 6 or claim 7, wherein the polymeric part is manufactured by a RAM extrusion process.

10. The method of any one of claims 1 to 9, wherein the hydrogen rich atmosphere within the container has approximately 30% to 100% hydrogen by volume.

11. A method for improving the wear resistance of a polymeric manufactured part, comprising the steps of:

providing one or more manufactured polymeric parts;
placing the parts in one or more sealable, gas impermeable packaging containers;
removing substantially all of the oxygen from within the packaging container;
pressurizing the packaging containers with an inert gas at a pressure greater than 1.5 to 4.0 atmospheres;
irradiating the pressurized containers and the polymeric parts for a period of time sufficient to sterilize the parts; and
following the step of irradiating, the method further comprises the step of ageing the polymeric parts within the atmosphere of the packaging container for a period of time.

12. A method for improving the wear resistance of a polymeric manufactured part, comprising the steps of:

providing one or more manufactured polymeric parts;
placing the parts in one or more sealable, gas impermeable packaging containers;
removing substantially all of the oxygen from within the packaging container;
pressurizing the packaging containers with a mixture of hydrogen gas and an inert gas at a pressure greater than 1.5 atmospheres;
irradiating the pressurized containers and the polymeric parts for a period of time sufficient to sterilize the parts; and
aging the part within the atmosphere of the irradiated packaging container for a period of time.

13. The method of claim 12, wherein the mixture of hydrogen gas and an inert gas is **characterized by** a minimum of 2.2×10^{-3} moles of hydrogen gas per gram of polymeric material within the packaging container and a volumetric concentration of hydrogen within the container in the range of 30% to 95%.

14. The method of any one of claims 11 to 13, wherein the part is aged within the packaging container for at least 48 hours.

15. The method of any one of claims 11 to 14, wherein the step of removing the oxygen from within the packaging containers is effected by flushing the container with an inert gas.

16. The method of any one of claims 11 to 14, wherein the step of removing the oxygen from within the packaging containers is effected by applying a vacuum force to the containers.

17. The method of any one of claims 11 to 16 wherein the inert gas is selected from the group consisting of argon, helium, and nitrogen.

18. The method of any one of claims 11 to 17, wherein the packaging container is rigid.

19. The method of any one of claims 11 to 17, wherein the packaging container is flexible.

20. The method of any one of claims 11 to 19, wherein the step of irradiating is carried out using gamma, x-ray, or electron beam radiation.

21. The method of claim 20, wherein the step of irradiating is carried out until a dose of 20-60 KGy has been achieved.

Patentansprüche

1. Verfahren zur Verbesserung der Verschleißfestigkeit eines auf Polymerbasis hergestellten Teils, umfassend die Schritte von
Bereitstellen eines oder mehrerer auf Polymerbasis hergestellter Teile;

Anordnen der Teile in einem oder mehreren gasundurchlässigen, flexiblen Verpackungsbehältern, wobei jeder Behälter zumindest eine heißsiegelfähige Öffnung darin aufweist;
Aussetzen des Verpackungsbehälters und der Polymerteile an eine Vakuumkraft;
Heißsiegeln des flexiblen Verpackungsbehälters, während er der Vakuumkraft ausgesetzt ist, und nach Versiegeln des Verpackungsbehälters Ausüben eines hydrostatischen Drucks auf das Teil;
Bestrahlen der heißversiegelten Verpackungen und der Teile unter Druck für eine Zeitspanne, die ausreichend ist, um die Teile zu sterilisieren; und
nachfolgend dem Schritt der Bestrahlung, Alterung der Polymerteile innerhalb der Atmosphäre des Verpackungsbehälters für eine Zeitspanne;
wobei die Vakuumkraft ausreichend ist, um im Wesentlichen den gesamten Sauerstoff aus dem Verpackungsbehälter zu entfernen, wobei die Vakuumkraft im Bereich von 500 bis 1013 mbar liegt.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** der hydrostatische Überdruck, der auf das Teil ausgeübt wird, im Bereich von 48 bis 101 kN/m^2 (7 bis 14,7 psig) liegt.

3. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** alles Gas innerhalb des flexiblen Verpackungsbehälters nach der Bestrahlung weniger als 2,2 x 10^{-5} mol/g an Wasserstoff aufweist.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** nachfolgend dem Schritt der Bestrahlung das Teil durch einen Gelgehalt im Bereich von 75 bis 100%, bestimmt durch das Verfahren C von ASTM D2765-90, charakterisiert ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** der flexible Verpackungsbehälter aus einer Metallfolie hergestellt ist, die von einer oder mehreren Lagen eines Polymerfilms umgeben ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** das Polymerteil aus einem Polymer gebildet ist, das aus der Gruppe umfassend Polyethylen mit geringer Dichte, Polyethylen mit hoher Dichte, Polyethylen mit extrem hohem Molekulargewicht, Polypropylen, Polyester, Nylon, Polyurethan und Poly(methylmethacrylat) ausgewählt ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** das Polymerteil aus einem Polyethylen mit extrem hohem Molekulargewicht, das ein zahlenmäßiges durchschnittliches molekulares Gewicht von größer als 1,0 Mio. aufweist, gebildet ist.

8. Verfahren nach Anspruch 6 oder 7, **dadurch gekennzeichnet, dass** das Polymerteil durch ein Pressverfahren hergestellt ist.

9. Verfahren nach einem der Ansprüche 6 oder 7, **dadurch gekennzeichnet, dass** das Polymerteil durch ein Kolbenstrangpressverfahren hergestellt wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** die wasserstoffreiche Atmosphäre innerhalb des Behälters einen Volumenanteil von 30% bis 100% Wasserstoff aufweist.

11. Verfahren zur Verbesserung der Verschleißfestigkeit eines auf Polymerbasis hergestellten Teils, umfassend die Schritte:

    Bereitstellen eines oder mehrerer auf Polymerbasis hergestellter Teile;
    Anordnen der Teile in einem oder mehreren versiegelbaren, gasundurchlässigen Verpackungsbehältern;
    Entfernen im Wesentlichen des gesamten Sauerstoffs aus dem Verpackungsbehälter; unter Druck setzen der Verpackungsbehälter innerhalb eines inerten Gases bei einem Druck, der größer als 1,5 bis 4,0 Atmosphären ist;
    Bestrahlen der unter Druck gesetzten Behälter und der Polymerteile für eine Zeitspanne, die ausreichend ist, um die Teile zu sterilisieren; und
    nachfolgend dem Schritt der Bestrahlung, umfasst das Verfahren ferner den Schritt der Alterung der Polymerteile innerhalb der Atmosphäre des Verpackungsbehälters für eine Zeitspanne.

12. Verfahren zur Verbesserung der Verschleißfestigkeit eines auf Polymerbasis hergestellten Teils, umfassend die Schritte von:

Bereitstellen eines oder mehrerer auf Polymerbasis hergestellten Teile;
Anordnen der Teile in einem oder mehreren versiegelbaren, gasundurchlässigen Verpackungsbehälter;
Entfernen im Wesentlichen des gesamten Sauerstoffs aus dem Verpackungsbehälter;
unter Druck setzen der Verpackungsbehälter mit einer Mischung aus Wasserstoffgas und einem inerten Gas bei einem Druck, der größer als 1,5 Atmosphären ist;
Bestrahlen der unter Druck gesetzten Behälter und der Polymerteile für eine Zeitspanne, die ausreichend ist, um die Teile zu sterilisieren; und
Alterung des Teils innerhalb der Atmosphäre des bestrahlten Verpackungsbehälters für eine Zeitspanne.

13. Verfahren nach Anspruch 12, **dadurch gekennzeichnet, dass** die Mischung aus Wasserstoffgas und einem inerten Gas durch einen minimalen Anteil von 2,2 x 10^{-3} mol an Sauerstoffgas pro g an Polymermaterial innerhalb des Verpackungsbehälters und eine Volumenkonzentration an Wasserstoff innerhalb des Behälters im Bereich von 30% bis 95% charakterisiert ist.

14. Verfahren nach einem der Ansprüche 11 bis 13, **dadurch gekennzeichnet, dass** das Teil innerhalb des Verpackungsbehälters für zumindest 48 Stunden gealtert wird.

15. Verfahren nach einem der Ansprüche 11 bis 14, **dadurch gekennzeichnet, dass** der Schritt des Entfernens des Sauerstoffs aus den Verpackungsbehältern durch Spülen des Behälters mit einem inerten Gas erreicht wird.

16. Verfahren nach einem der Ansprüche 11 bis 14, **dadurch gekennzeichnet, dass** der Schritt des Entfernens des Sauerstoffs aus den Verpackungsbehältern durch Anwendung einer Vakuumkraft auf die Behälter erreicht wird.

17. Verfahren nach einem der Ansprüche 11 bis 16, **dadurch gekennzeichnet, dass** das inerte Gas aus einer Gruppe umfassend Argon, Helium und Stickstoff, ausgewählt ist.

18. Verfahren nach einem der Ansprüche 11 bis 17, **dadurch gekennzeichnet, dass** der Verpackungsbehälter steif ist.

19. Verfahren nach einem der Ansprüche 11 bis 17, **dadurch gekennzeichnet, dass** der Verpackungsbehälter flexibel ist.

20. Verfahren nach einem der Ansprüche 11 bis 19, **dadurch gekennzeichnet, dass** der Schritt des Bestrahlens unter Verwendung von Gamma-, Röntgen- oder Elektronenstrahlstrahlung ausgeführt wird.

21. Verfahren nach Anspruch 20, **dadurch gekennzeichnet, dass** der Schritt der Bestrahlung durchgeführt wird, bis eine Dosis von 20 bis 60 KGy erreicht worden ist.

Revendications

1. Procédé d'amélioration de la résistance à l'usure d'une partie fabriquée en polymère, comprenant les étapes :

d'apporter une ou plusieurs parties fabriquées en polymère ;
de placer les parties dans un ou plusieurs réservoirs d'emballage flexibles, imperméable aux gaz, chaque réservoir possédant au moins une ouverture scellable thermiquement ;
de soumettre le réservoir d'emballage et les parties en polymère à une force de vide;
de sceller thermiquement le réservoir d'emballage flexible alors qu'il est soumis à une force de vide et après scellement du réservoir d'emballage, d'exercer une pression hydrostatique sur la partie ;
d'irradier l'emballage scellé thermiquement et les parties sous pression pendant une durée de temps suffisante pour stériliser les parties ; et
suite à l'étape d'irradiation, vieillissement des parties polymère dans l'atmosphère du réservoir de l'emballage

pendant une période de temps ;

dans lequel la force de vide est suffisante pour éliminer en grande partie tout l'oxygène à l'intérieur du réservoir de l'emballage ;
la force de vide étant dans le domaine de 500-1013 mbars

2. Procédé selon la revendication 1, **caractérisée en ce que** la pression hydrostatique de la jauge exercée sur la partie est dans le domaine de 48 à 101 KN/m^2 (7 à 14,7 psig).

3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** tout gaz contenu dans le réservoir d'emballage flexible, après irradiation, contient moins de 2,2 x 10^{-5} mole/g d'hydrogène.

4. Procédé selon l'une quelconque des revendications 1 à 3, **caractérisé en ce que**, suite à l'étape d'irradiation, la partie est **caractérisée par** un contenu en gel dans le domaine de 75 à 100 % tel que déterminé par la méthode de la norme ASTM D2765-90.

5. Procédé selon l'une quelconque des revendications 1 à 4, **caractérisé en ce que** le réservoir de l'emballage flexible est fabriqué avec une feuille métallique qui est entourée par une ou plusieurs couches d'un film polymère.

6. Procédé selon l'une quelconque des revendications 1 à 5 **caractérisé en ce que** la partie est fabriquée avec un polymère choisi, dans le groupe comprenant du polyéthylène basse densité, du polyéthylène haute densité, du polyéthylène de masse moléculaire très élevée, du polypropylène, du polyester, du nylon, du polyuréthanne, et du poly(méthylméthacrylate).

7. Procédé selon l'une quelconque des revendications 1 à 6, **caractérisé en ce que** la partie polymère est fabriquée avec un polyéthylène de masse moléculaire très élevée ayant une masse moléculaire moyenne en nombre supérieure à 1,0 million.

8. Procédé selon la revendication 6 ou la revendication 7, **caractérisé en ce que** la partie polymère est fabriquée par un procédé de moulage par compression.

9. Procédé selon la revendication 6 ou la revendication 7, **caractérisé en ce que** la partie polymère est fabriquée par un procédé d'extrusion RAM.

10. Procédé selon l'une quelconque des revendications 1 à 9, **caractérisé en ce que** l'atmosphère riche en hydrogène dans le réservoir contient de 30 % à 100 % d'hydrogène en volume.

11. Procédé d'amélioration de la résistance à l'usure d'une partie fabriquée en polymère, comprenant les étapes :

d'apporter une ou plusieurs parties fabriquées en polymère ;
de placer les parties dans un ou plusieurs réservoirs d'emballage flexibles, imperméable aux gaz,
d'éliminer en grande partie tout l'oxygène du réservoir d'emballage;
de mise sous pression les réservoirs d'emballage ;
de soumettre les réservoirs d'emballage avec un gaz inerte à une pression supérieure de 1,5 à 4,0 atmosphères ;
d'irradiation des réservoirs pressurisés et des parties en polymère pendant une durée de temps suffisante pour stériliser les parties ; et
suite à l'étape d'irradiation, le procédé comprend en plus l'étape de vieillissement des parties polymère dans l'atmosphère du réservoir d'emballage pendant une période de temps.

12. Procédé d'amélioration de la résistance à l'usure d'une partie fabriquée en polymère, comprenant les étapes :

d'apporter une ou plusieurs parties fabriquées en polymère;
de placer les parties dans un ou plusieurs réservoirs d'emballage flexibles, imperméable aux gaz ;
d'éliminer en grande partie tout l'oxygène du réservoir d'emballage ;
de mise sous pression des réservoirs d'emballage avec un mélange d'hydrogène gazeux et d'un gaz inerte à une pression supérieure à 1,5 atmosphères
d'irradiation des réservoirs pressurisés et des parties en polymère pendant une durée de temps suffisante

pour stériliser les parties ; et
vieillissement de la partie polymère dans l'atmosphère de l'emballage irradié pendant une période de temps.

13. Procédé selon la revendication 12, **caractérisé en ce que** le mélange d'hydrogène gazeux et de gaz inerte contient un minimum de 2,2 x 10^{-3} moles d'hydrogène gazeux par gramme de matériau polymère dans le réservoir d'emballage et une concentration volumétrique d'hydrogène dans le réservoir dans le domaine de 30 % à 95 %.

14. Procédé selon l'une quelconque des revendications 11 à 13, **caractérisé en ce que** la partie polymère est vieillie dans le réservoir d'emballage pendant au moins 48 heures

15. Procédé selon l'une quelconque des revendications 11 à 14, **caractérisé en ce que** l'étape d'élimination de l'oxygène des réservoirs d'emballage est effectuée par purge du réservoir avec un gaz inerte.

16. Procédé selon l'une quelconque des revendications 11 à 14, **caractérisé en ce que** l'étape de l'élimination de l'oxygène des réservoirs d'emballage est effectuée par application d'une force de vide sur les réservoirs.

17. Procédé selon l'une quelconque des revendications 11 à 16 **caractérisé en ce que en ce que** le gaz inerte est choisi dans le groupe comprenant l'argon, l'hélium et l'azote.

18. Procédé selon l'une quelconque des revendications 11 à 17, **caractérisé en ce que** le réservoir d'emballage est rigide

19. Procédé selon l'une quelconque des revendications 11 à 17, **caractérisé en ce que** le réservoir d'emballage est flexible.

20. Procédé selon l'une quelconque des revendications 11 à 19, **caractérisé en ce que** l'étape d'irradiation est effectuée en utilisant des radiations gamma, rayons X et faisceau d'électrons.

21. Procédé selon la revendication 20, **caractérisé en ce que** l'étape d'irradiation est effectuée jusqu'à ce qu'une dose de 20-60 KGy soit atteinte.

FIG.1

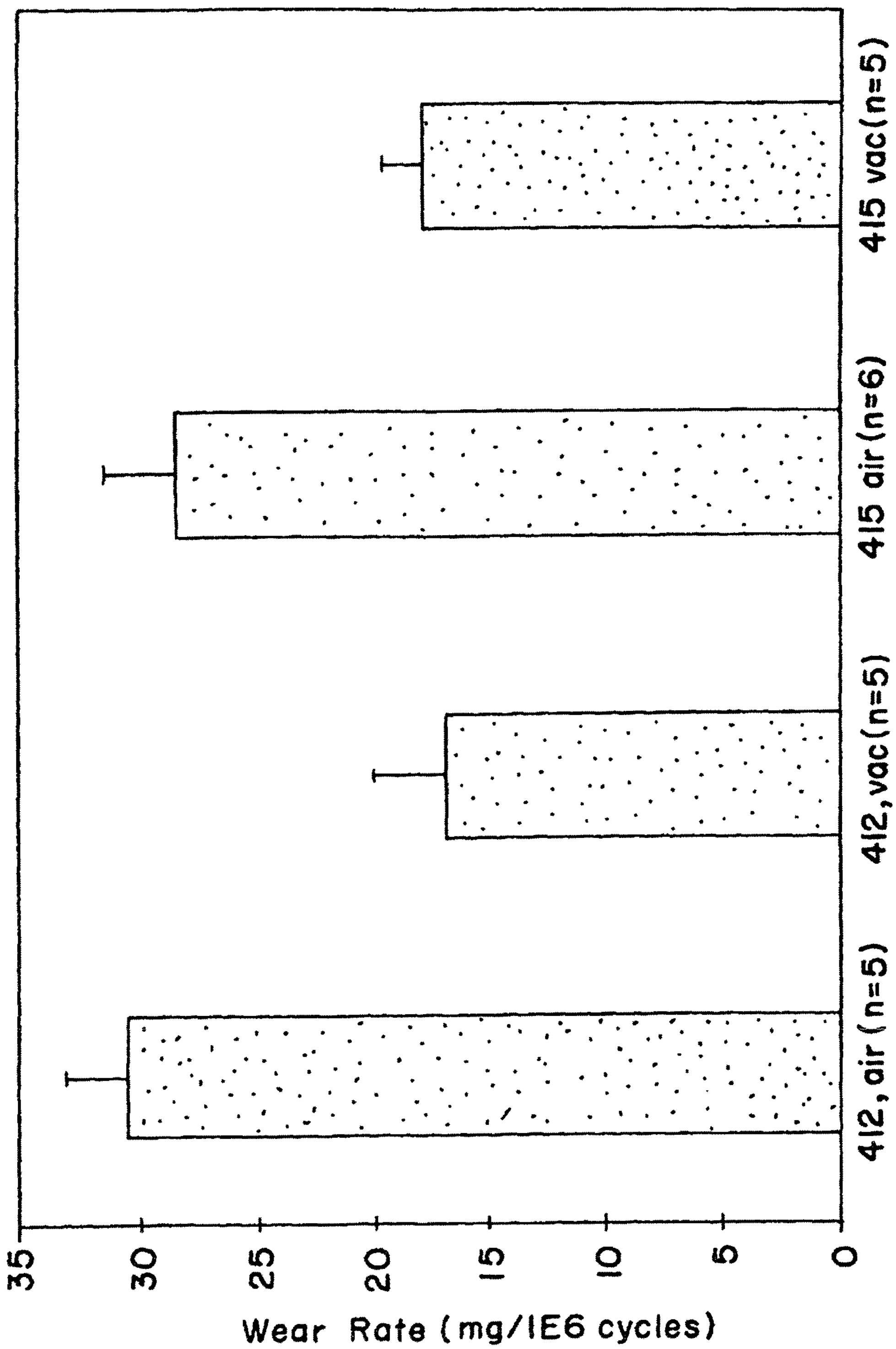
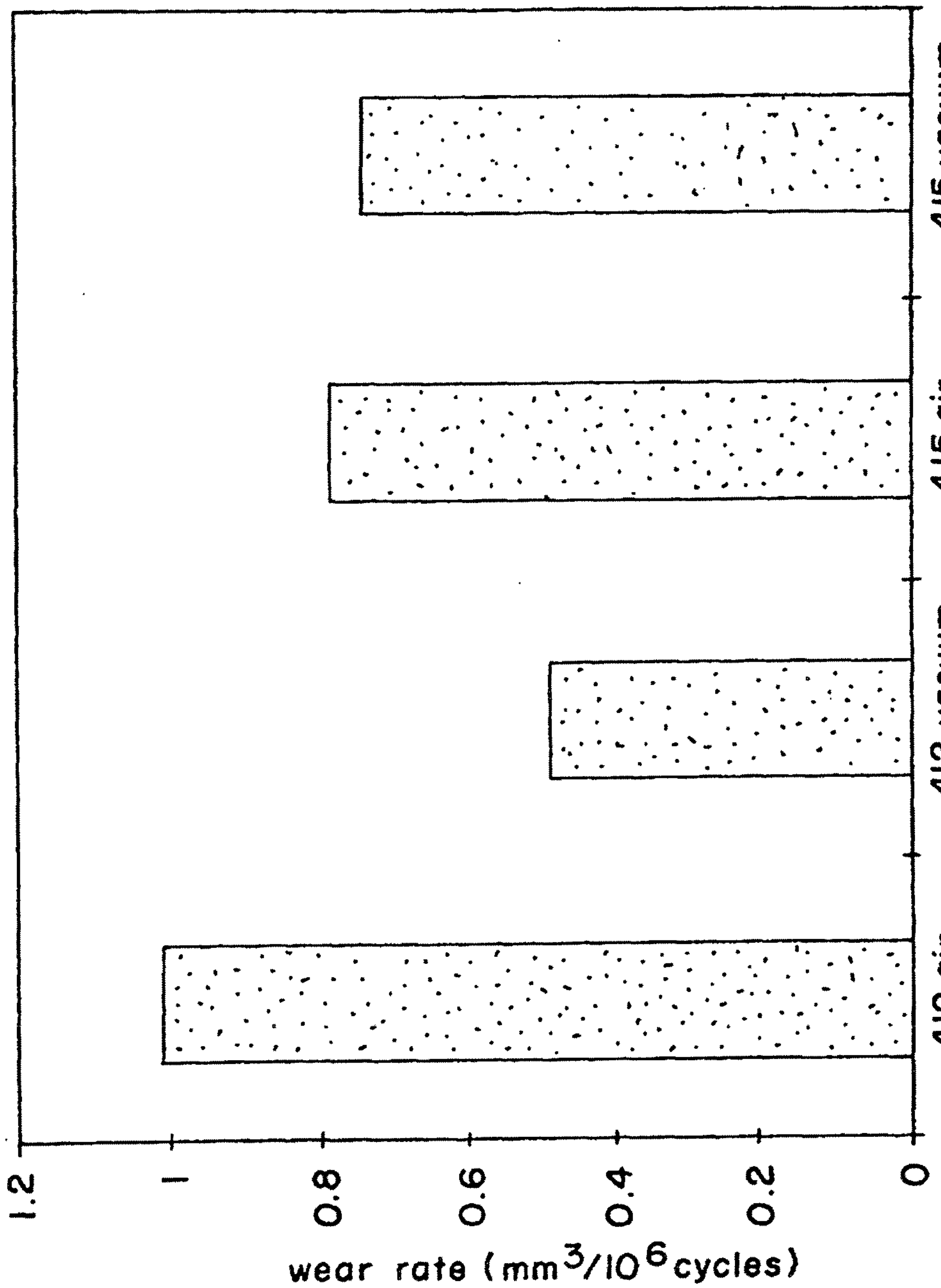

412, air (n=5)
412, vac (n=5)
415 air (n=6)
415 vac (n=5)
0
5
10
15
20
25
30
35
Wear Rate (mg/1E6 cycles)

FIG.2


412 air
412 vacuum
415 air
415 vacuum
1.2
1
0.8
0.6
0.4
0.2
0
wear rate (mm3/10 6 cycles)

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1R314C1C 1R314C1F
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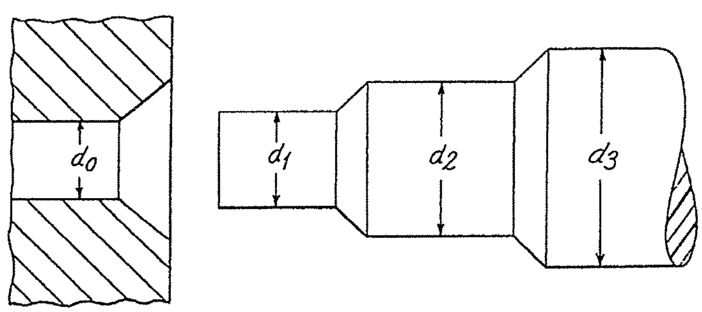
(54) Drawing Thermoplastics Material

(57) Oriented thermoplastics having enhanced properties such as Young's modulus, resistance to creep, resistance to gas transport are prepared by drawing the thermoplastics in the solid phase through a die so that its plastic strain is progressively increased during start-up. This can be effected by providing a progressively reduced cross-section at the end of the workpiece to which draw tension is to be applied, e.g. the end may be conical, or reduced in steps as in Fig. 3.

Fig. 3



$$R_{Ni} = \left(\frac{d_i}{d_0}\right)^2$$

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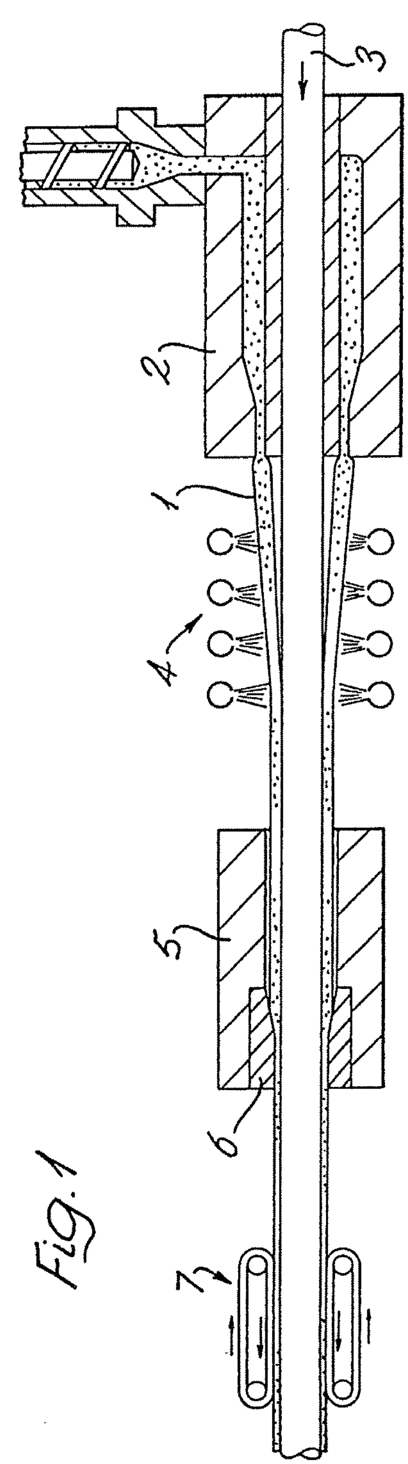


Fig. 1

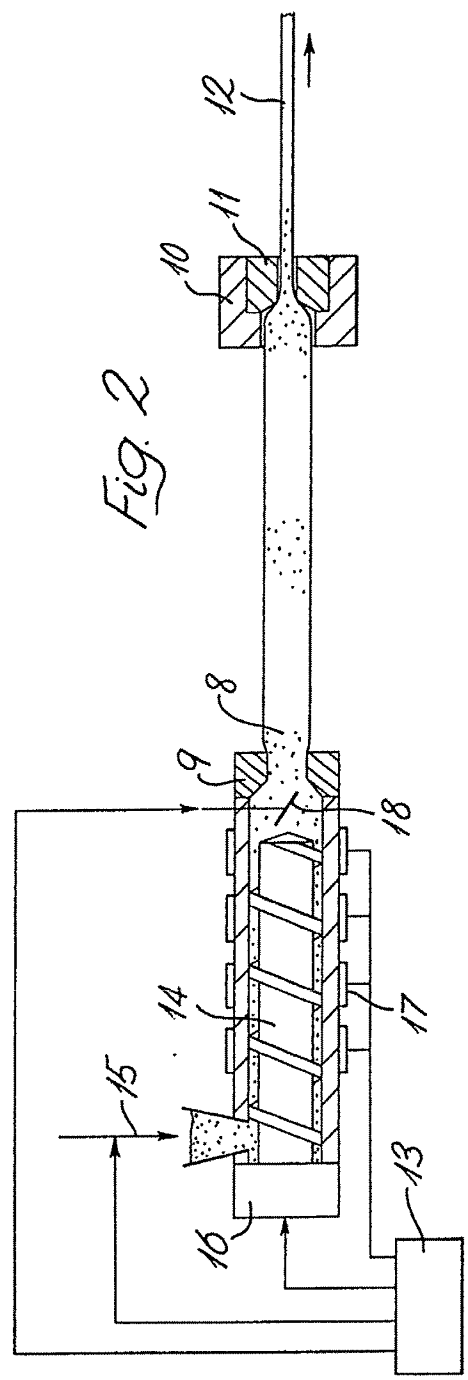
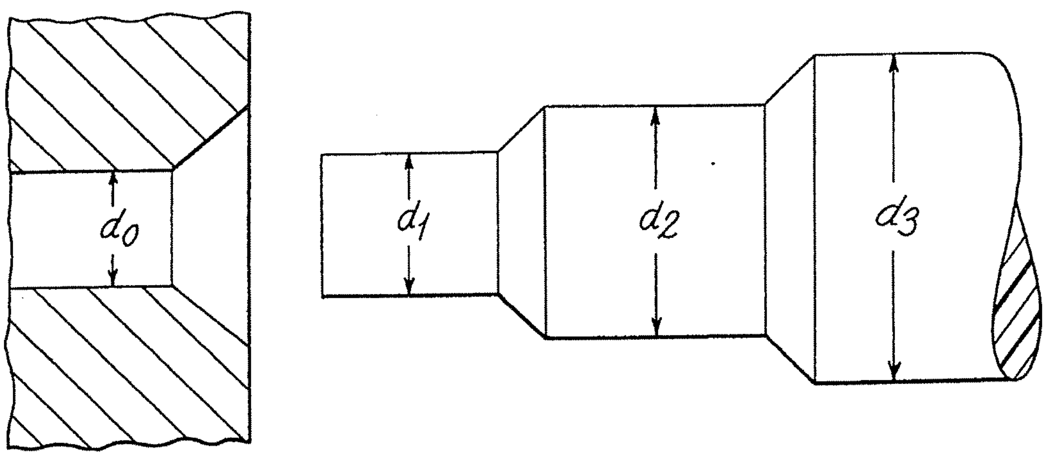


Fig. 2

Fig. 3



$$R_{Ni} = \left(\frac{d_i}{d_0}\right)^2$$

SPECIFICATION
Polymer Processing

This invention relates to the deformation of thermoplastic polymers; more particularly, this invention relates to the solid phase deformation and concomitant orientation of orientable, thermoplastic polymers.

U.K. Patent No. 1311885 discloses a process for reducing the cross-sectional area of an article of an orientable, thermoplastic polymeric material by drawing the article, at a temperature below its melting point, through a well-lubricated die of smaller cross-sectional area than that of the article, which process comprises forming an integral, preferantially oriented nose at one end of the article by a solid phase deformation process, such that the tensile strength of the nose exceeds the draw tension to be applied to the article, gripping the nose and drawing the article through the die so as to induce a substantial degree of molecular orientation throughout the drawn article.

This patent specification further discloses that the process is preferably performed by utilising the technique of hydrostatic extrusion; indeed, every example of the invention does use this technique. However, and as the specification rightly points out, at the date of the specification simple hydrostatic extrusion was limited by a deformation ratio "boundary" above which further increase in the ratio of the cross-sectional area of the polymer billet to that of the extruder die orifice had no useful effect; relaxation effects resulted in an extrudate exhibiting die swell limiting the actual deformation ratio and orientation. These "boundaries" are given as low as 2.1:1 for polyvinyl chloride to 5.8:1 for glass fibre-filled polypropylene. The specification discloses overcoming this disadvantage by applying to the issuing extrudate a deforming draw tension, the complete process often being referred to as draw assisted extrusion.

U.K. Patent No. 1480479 discloses a process for the production of an oriented polymer material which comprises preparing a polymeric workpiece by cooling a semi-crystalline polymer having a natural draw ratio greater than 6 from the melt at a rate from 0.1 to 10°C per minute thereby obtaining the workpiece with substantially uniform morphology in cross-section; and deforming the workpiece below the melting point of the polymer by application of pressure.

This patent specification further discloses that by starting with a polymer of seleced weight and number average molecular weights and thermal history it is possible to increase the deformation ratio "boundaries" to much higher levels. Moreover, at deformation ratios greater than about 8:1, and contrary to the teaching of U.K. 1311885, it is disclosed that die swell with lowered actual deformation is not encountered and thus, as is shown in Examples 2 and 3, the application to the issuing extrudate of a deforming draw tension is unnecessary.

According to the present invention, there is provided a process for the solid phase deformation of a workpiece of an orientable thermoplastic polymer, which process comprises: providing the workpiece of the essentially unoriented polymer at the entry side of a die; applying to the workpiece from the exit side of a die a draw tension insufficient to cause tensile failure of the workpiece; and drawing the workpiece through the die so that its plastic strain is progressively increased during start-up of the process.

The term "workpiece" as used herein includes bars, strips, rods, multifilaments, tubes and other cross-sections of solid or hollow stock. The term includes both billets and other forms of stock of greater length; indeed, continuous stock, which may be formed as the process is performed, may be utilised: examples include a polymer sheathed continuous core such as a metal wire, or continuous polymer rod, film or filaments.

The orientable thermoplastic polymer is desirably a semi-crystalline polymer, especially one which exhibits sufficient strain hardening and strain rate dependence of the flow stress to stabilise the neck formed under the desired drawing conditions. Preferred such polymers are unsubstituted or fluoro-substituted vinyl polymers and polyacetals, suitably a linear homo- or copolymer of ethylene or propylene with at least one comonomer, a vinylidene fluoride polymer or a homo- or co-polyoxymethylene.

Where it is intended to utilise the die drawing process of this invention to produce a product with enhanced Young's modulus; resistance to creep; resistance to gas transport; enhanced deadfold; or enhanced axial thermal conductivity then a workpiece of a linear homo- or copolymer of ethylene should desirably comprise a polymer having a weight average molecular weight ($\bar{M}_w$ less than 1,000,000, suitably from 50,000 to 500,000, preferably from 70,000 to 400,000; one of a linear homo- or copolymer of propylene should desirably comprise a polymer having a $\bar{M}_w$ from 150,000 to 800,000, preferably from 250,000 to 500,000.

However, the die drawing process of this invention may also be performed, to provide a more advantageous forming process but not the enhanced properties listed above, on a workpiece of an essentially unoriented but orientable, amorphous polymer or an essentially unoriented but orientable, semi-crystalline ultra high molecular weight polymer (for example, a linear homopolymer of ethylene having a $\bar{M}_w$ about 2,000,000). It may likewise be utilised, but to a lower deformation ratio, in respect of those polymers which would otherwise give the enhanced properties listed above.

The thermoplastic polymer workpieces used in the process of this invention may be filled. Examples of useful fibrous fillers include glass, asbestos, metal carbon and ceramic whiskers, such as those formed from silicon carbide. Examples of useful laminar fillers include mica,

talc and graphite flakes. Chalk and fly ash may also be included. The amount of filler which may advantageously be included depends on the nature of the filler, but up to 50% by weight, preferably less than 30%, especially less than 20% may be incorporated.

The term "essentially unoriented" as used herein means the workpiece has incurred no orientation other than that minor amount which might be induced during formation of the workpiece, for example during billet moulding or melt extrusion, or during any subsequent shaping thereof, for example by machining, prior to the performance of the die drawing process of this invention.

Where it is not possible to use the polymer as received as a workpiece, the workpiece may be formed either in the batch or continuously. In either case, where the cross-sectional area of the workpiece is substantially greater than that, for example, of a textile filament care must be taken to ensure that the workpiece cools sufficiently slowly to prevent voids and stress cracking from occurring. At low cross-sectional area, surface cooling effects outweigh bulk conduction effects and the formation of voids and cracks is not found to pose any problem. Indeed, it is envisaged that the process of the invention applied to a workpiece, particularly a continuous workpiece, of low cross-sectional area, such as a filament or a film, will provide a practicable alternative to melt spinning or melt extrusion techniques for producing such material with enhanced Young's modulus.

In the case of a workpiece formed in the batch, for example a polymer billet, the following general methods have been found to be suitable. The polymer may be melted in a screw extruder; extruded or injected into a billet mould at a temperature about 30°C above its melting point and cooled under elevated pressure for 5 hours, or it may be melted in an extruder; extruded or injected into a cold billet mould; transferred to an oven for 4 hours under ambient pressure at a temperature below its melting point but above its crystallisation temperature; and thereafter allowed to cool in the oven after the heating has been switched off. The polymer may also be injection moulded into an air or water cooled billet mould. Progressive immersion in the cooling fluid is preferred, thereby ensuring that solidification of the polymer takes place from the bottom of the mould thereby preventing the formation of internal voids due to shrinkage. Where the workpiece is to be hollow it may be formed in the batch by including a mandrel of appropriate cross-section, usually coaxially, in the mould. Alternatively stock of circular solid or hollow cross-section may be produced continuously using one of several processes known to those skilled in the art.

In accordance with the die drawing process of this invention the plastic strain of the workpiece is progressively increased during start-up of the process. This can be effected, in accordance with one embodiment of the invention, by utilising a workpiece wherein that end (herein termed the "nose") of the workpiece to which the draw tension is applied is of progressively reduced (either continuously or in stages) cross section. (Hereinafter particular reference is made for convenience to stock or circular solid or hollow cross-section. The die drawing process of this invention is not, however, limited to such cross-sections). The first alternative may be affected either by fabricating the workpiece with a conical nose, for example, by machining the workpiece to form a conical nose, or moulding the billet with a conical nose. The semi-angle of the nose should be less than that of the die through which the workpiece is to be drawn. The second alternative may be effected by fabricating, for example by machining the workpiece so that it has at least one, and preferably a plurality, for example from 2 to 4, of stages of progressively reduced cross-section, which together form a nose as shown in Figure 3 of the accompanying drawing.

In accordance with another embodiment of the invention the plastic strain of the workpiece can be progressively increased by providing at the entry side of the die a workpiece of essentially uniform cross section and, during start-up of the process, progressively reducing the aperture of the die orifice.

Both such embodiments may be effected simultaneously.

In both such embodiments, the nose is advanced to protrude through the die lips and is secured to tensioning means applied from the exit side of the die. A suitable arrangement includes a hauloff comprising a pair of serrated jaws in which the nose is gripped; a high tensile cable one end of which cable is attached to the jaws, the other to a winch or a loading station to which a turning moment or mass may be applied thereby applying a draw tension to the nose. The hauloff may also comprise, instead of a cable, any tension transmitting means such in the metal drawing art including a chain, a rack and pinion mechanism, a screw mechanism and a hydraulically operated draw mechanism. The hauloff may further comprise a pair of continuous contra-rotating friction belts, generally known as a "caterpillar".

The draw tension should be sufficient to draw the workpiece through the die but insufficient to cause tensile failure of the article; that is, the draw tension should be such that the true stress at any point of the product does not exceed its fracture stress at that point. A suitable maximum value of drawn tension may readily be determined by routine experiment. In the case of strain hardening polymers, as the drawing progresses the flow stress of the strained portions of the workpiece increases. This will permit a greater draw tension to be applied (giving an increased plastic strain). This enables greater cross-sections of workpiece, or smaller apertures of die, or both, to be utilised also giving a further increase in plastic strain. These increases further strengthened

the strained polymer so that the strain can be progressively increased during start-up until a product having desired final properties (for example, Young's modulus or cross-sectional area) is attained whereafter steady state processing conditions obtain.

After a grippable length of the workpiece has been drawn through the die the unoriented part of its nose may be removed and the oriented grippable length re-gripped thereby enabling a higher load to be applied.

For a particular polymer, a steady state process is obtained for a given set of temperature, draw speed and deformation ratio. "Deformation ratio" as used herein is the ratio of the initial cross-sectional area of the workpiece to the final cross-sectional area of the product. These parameters vary implicitly, but it has been found possible, for a particular polymer, to set the die temperature (which will be only a nominal temperature for the polymer since the process is not an isothermal one) and the workpiece shape and vary, by experiment, the draw speed to obtain the desired deformation ratio.

For linear homo- and copolymers of ethylene the die temperature is desirably set within 60°C below the melting point of the polymer, More particularly, for such polymers of $\bar{M}_w$ from 50,000 to 150,000, the die temperature is preferably from 70°C to 100°C; and for such polymers of $\bar{M}_w$ above 300,000 from 70°C to 120°C; For linear homo- and copolymers of polypropylene of weight average molecular weight from 150,000 to 800,000 the die temperature may be set from 20°—170°C, preferably 90°—130°C. A die temperature of 80°—170°C, preferably 150°—170°C is suitable for homo- or copolyoxymethylene and of 80°C to 165°C is suitable for vinylidene fluoride polymers. The polymer temperature may be further controlled by utilising a die with a temperature controlled chamber which extends downstream.

It is feasible to use draw speeds greater than 1 cm min^{-1} in the die drawing process of this invention; indeed, speeds of 50 cm min^{-1} or more are preferred.

Where hollow stock is being die drawn by the process of this invention it is essential to provide an appropriately dimensioned mandrel on the entry side of the die and protruding between the die lips to prevent collapse. In a continuous process this mandrel can suitably be of the "floating plug" type. In a batch process a fixed mandrel may be used.

A batch process may be converted to a continuous one by putting the upstream end of the deforming workpiece and the downstream end of stock of the same cross-section both in contact with a hot, stainless steel plate; removing the plate and welding the two polymer surfaces. Preferably such a weld should be at an angle of 45° or less to the axis of the stock.

Utilising the die drawing process of this invention in polymers which show adequate strain hardening and strain rate dependence of the flow stress, it is possible to obtain deformation ratios of at least 10, preferably 20 or even more.

The invention will now be more particularly described, by way of example, with reference to the accompanying drawings in which:

Figure 1 represents an axial section of a coextrusion line in accordance with the invention; and

Figure 2 represents an axial section of an automated continuous extrusion line in accordance with the invention.

In Figure 1, a polymer coating 1 is supplied as melt flow from an extruder fitted with a crosshead annular die 2 through the centre of which the member to be coated 3 (such as cable, wire, rod or tube) is allowed to pass. The melt then passes through a cooling zone 4 where it is solidified. At the end of this zone the solidified coating 1 is essentially isotropic and is not in intimate contact with the surface of the member to be coated 3. Both member and isotropic coating then pass into a drawing block 5 of similar design to that already described and are heated to the drawing temperature. The polymer coating is next drawn through the converging die 6 mounted in the drawing block. Deformation of the polymer continues beyond the drawing block for some distance before it becomes "frozen-out". At this stage both member and coating are travelling with the same velocity, and the coating in intimate contact with the member. The velocity of the process is controlled and determined by a haul-off "caterpillar" device 7 situated downstream from the final deformation zone.

The ratio of the cross-sectional area of the isotropic polymer tube entering the die block to that of the annular clearance between coated member and die bore is of great importance, as will be understood from the foregoing description of the process. This ratio is controlled and determined by the rate of output of the melt extruder which supplies the crosshead die. This embodiment of the invention can be used to coat several items simultaneously; used where the cross-section is not circular; or used where two or more different polymers are co-extruded.

In Figure 2 a polymer billet 8 is continuously extruded through a die 9 as described in British patent application 15023/79. The billet is then advanced to a drawing block 10 and drawn by a haul-off device (not shown) through a converging die 11 mounted in the drawing block. The haul-off velocity and the temperatures of the billet 8 and the drawn product 12 are continuously monitored; their values being input into a computer 13 whence output regulating the melt extrusion rate and quality given by the extruder 14 is provided to the hopper feed 15, the screw drive 16, the barrel heater 17 and the infinitely variable orifice controlled by butterfly valve 18.

In accordance with a further aspect of this invention, there are provided homo- and copolymers of polypropylene which have been deformed by passage through a die in the solid phase having a Young's modulus greater than 18,

suitably greater than 20, preferably greater than 23 GPa, especially greater than 25 GPa. This invention further provides a homo or copolyoxymethylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 25 GPa, preferably greater than 27 GPa. This invention further provides a vinylidene fluoride polymer which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 3 GPa, suitably greater than 5 GPa preferably greater than 8 GPa. This invention also provides copolymers of linear polyethylene, particularly copolymers comprising a minor amount of hexene-1, especially those which have been deformed by passage through a die in the solid phase, having a Young's modulus greater than 30 GPA, preferably greater than 40 GPa. Such copolymer materials cannot be produced at high deformation ratios by conventional drawing or solid state extrusion. This invention further provides a Portland cement or concrete mass incorporating fibres either prepared as such or by fibrillating a film prepared by the process of this invention, particularly fibres of an ethylene-hexene-1 copolymer.

The advantages of the die drawing process of this invention over hydrostatic extrusion will be manifest to those skilled in the art. Thus, it obviates the necessity of a batch process and dispenses with expensive and potentially hazardous pressure equipment. It is also found that, and in contrast to hydrostatic extrusion, throughput increases with increasing deformation ratio.

The following Examples illustrate the invention.

Modulus values were determined from a flexural (three-point bend) test at 20°C. This was accomplished by applying a dead load to the test specimen and measuring the deflection after 10 seconds. The ratio of span to specimen thickness was maintained at 80 or higher. The maximum strain at any point in the specimen was less than 0.001.

Example 1

A polypropylene block copolymer having weight average molecular weight of 650,000 (PROPATHENE GSE 108 *ex* I.C.I.) was melted at 250°C in an extruder; extruded into a billet mould at 160°C; and cooled under elevated pressure for 5 hours. The initial, isotropic billet was then machined so that the dimensions shown in the Figure in the accompanying drawing are:

$$d_1=7\text{mm},\ d_2=10.4\text{mm},\ d_3=15.8\text{mm}$$

The machined billet was then advanced into a conical die of 15° semi-angle and at a temperature set at 110°C. The die had a bore diameter of 7mm so that the nominal deformation ratios shown in Figure 3 of the accompanying drawings are:

$$R_{N1}=1,\ R_{N2}=2.2,\ R_{N3}=5.1$$

The protruding nose of the billet formed by the first stage was gripped at the exit side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at a speed of 10mm min^{-1} at a tension of 32.5 kg wt until all of the second stage had been drawn. The grip was then repositioned on part of the billet corresponding to the second stage and drawing recommenced, until sufficient of the third stage had been drawn through the die to enable the grip to be affixed thereto, at a draw speed of 10mm min^{-1} at a tension of 92.5 kg wt. Thereafter the grip was finally positioned on the drawn part of the third stage and the remainder thereof was drawn through the die at a draw speed of 500mm min^{-1} at a tension of 152 kg wt to give an oriented rod of actual deformation ratio 12.7 (average diameter 4.45mm) and a flexural Young's modulus of 15.1 GPa (±1.4 GPa).

In similar experiments a modulus of 20.6 GPa (±2.0 GPa) was achieved.

Example 2

Example 1 was repeated using a high density polyethylene homopolymer of $\bar{M}_w$ 312,000, $\bar{M}_w$ 33,000 (HO20—54P *ex* BP Chemicals). The machined billet had d_1=5 mm, d_2=8.9 mm and d_3=12.0mm and was drawn through a conical die of 15° semi-angle with its temperature set at 100°C. The die had a bore of 5.3 mm so that $R_{N1}=1$, $R_{N2}=2.8$ and $R_{N3}=5.2$. The respective draw speeds and tensions were 10mm min^{-1} at 22 kg wt; 10mm min^{-1} at 55 kg wt and 500mm min^{-1} at 78 kg wt.

The oriented rod had an actual deformation ratio of 10 (average diameter 3.88mm) and a flexural Young's modulus of 14 GPa.

Example 3

Example 1 was repeated using polyoxymethylene of $\bar{M}n$ 45,000 and $\bar{M}w/\bar{M}n$ slightly greater than 2 (Delrin 500 *ex* Du Pont). The die had its temperature set at 160°C.

The oriented rod had an actual deformation ratio of 12.6 and a flexural Young's modulus of 20 GPa.

Example 4

A high density polyethylene homopolymer of $\bar{M}w$ 135,000, $\bar{M}n$ 25,500 and melt flow index of 0.6 dg min^{-1} (006—60 *ex* BP Chemicals) was injection moulded using a mould with a 10mm diameter cylindrical cavity. The barrel temperature was 190°C, and the mould temperature was 110°C. The mould was held under injection pressure for 10 minutes to allow cooling and solidification to take place.

The initial isotropic billet had a diameter of 7mm one end of which was machined to give an essentially conical nose of 5° semi-angle which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machine billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die, the drawing was stopped and the product was cut off 20mm from the die. The oriented material protruding from the exit sde of the die was then regripped and drawing was recommenced at 5mm min^{-1}. The load rose to 22kg and remained constant thereafter. The draw speed was then increased progressively to 66mm min^{-1}.

An oriented rod of actual deformation ratio 23.5 and a flexural Young's modulus of 51 GPa was obtained.

Example 5

A high density polyethylene homopolymer (HO20—54P *ex* BP Chemicals) was compression moulded as follows; a two-part mould was filled with polymer powder, heated to 210°C and left for 20 minutes to attain thermal equilibrium. The mould was then placed between the platens of a press and the powder compressed into a cavity of dimensions 20mm×20mm×200mm. A force of 1200 KN was used. The platens were then water cooled and moulding pressure maintained until the mould temperature had fallen below 80°C.

The initial isotropic billet had a diameter of 12mm one end of which was machined to give an essentially conical nose of 5° semi-angle which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 100°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die.

The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 40 kg. The draw speed was then progressively increased to a steady state value of 77 kg.

An oriented rod of actual deformation ratio 11.2 and a flexural Young's modulus of 13 GPa was obtained.

Example 6

A high density polyethylene homopolymer of $\bar{M}_w$ about 3,500,000 (Hostalen GUR *ex* Hoechst) was used as received as isotropic rod stock of 8mm diameter. One end of this was machined to give an essentially conical nose of 5° semi-angle which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 130°.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 130°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 4kg. The draw speed was then gradually increased to 200mm min^{-1}. The load rose to a steady state value of 20kg.

An oriented rod of actual deformation ratio 5 and a flexural Young's modulus of 1.76 GPa was obtained.

Example 7

A copolymer of ethylene and hex-1-ene of $\bar{M}_w$ 155,000, $\bar{M}_n$ 16,900 and 0.9 to 1.5 n-butyl branches per 10^3 carbon atoms (002—55 *ex* BP Chemicals) was extrusion moulded in the following manner:

A melt extruder was used to fill a cylindrical aluminium mould, which was then placed vertically in an oven to allow solidification of the polymer. A temperature gradient was maintained in the oven so that the bottom of the mould was at 110° and the top at 120°C. This procedure ensured that solidification of the polymer took place from the bottom of the mould upwards, preventing the formation of internal voids due to shrinkage.

The initial, isotropic billet had a diameter of 9mm one end of which was machined to give an essentially conical nose of 5° semi-angle which was extended as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 100°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20 mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 31kg. The draw speed was then gradually increased to a steady state of 25mm min^{-1}.

An oriented rod of actual deformation ratio 27 and a flexural Young's modulus of 62 GPa was obtained.

Example 8

A high density polyethylene homopolymer (006—60 *ex* BP Chemicals) was injection moulded using a mould with a cylindrical cavity. The barrel temperature was 190°C and the mould temperature was 110°C. The mould was held under injection pressure for 10 minutes to allow solidification to take place.

The initial, isotropic tube billet was machined from the moulding. The tube billet had an internal

diameter of 2mm and an external diameter of 8mm. An essentially conical nose of 5° semi-angle which was extended as a tube with an outer diameter of 4mm for gripping purposes was machined on one end of the billet surface.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C. A fixed mandrel of 2mm diameter was then inserted into the billet.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 100°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die the drawing was stopped and the product cut of 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing recommenced. The load rose to 30kg. The draw speed was then progressively increased to a steady value of 50mm min^{-1}. The load increased to a steady state value of 31kg.

An oriented tube of actual deformation ratio 13 and a flexural Young's modulus of 23 GPa was obtained.

Example 9

A polypropylene copolymer (PROPATHENE GSE 108 *ex* I.C.I.) was extrusion moulded into a tube billet mould.

The procedure of Example 8 was then essentially repeated with the internal diameter of the tube billet 2mm, the external diameter 7.17mm. The initial temperature of the polymer was 110°C and the steady state draw speed was 40mm min^{-1}.

An oriented tube of actual deformation ratio 6.5 and a flexural Young's modulus of 6.3 GPa was obtained.

Example 10

Twenty-four filaments of a high density polyethylene homo- polymer of $\bar{M}_w$ 102,000, $\bar{M}_n$ 6,200 (Rigidex 50 *ex* BP Chemicals) were melt spun into a glycerol bath at 118°C. The isotropic filaments had a diameter of 1.36mm. Each filament was necked by contact with a hot stainless steel plate and the necked tow was then inserted into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding tow was then gripped at the exit side of the die and, at an initial temperature of 100°C, was drawn through the die at a draw speed which was progressively increased to a steady state value of 100mm min^{-1}.

An oriented tow of filaments of polygonal cross-section and deformation ratios of from 15 to 20 was obtained. The flexural Young's modulus of individual filaments was from 32 to 40 GPa.

Example 11

A polymer composite containing 75% polypropylene ("Propathene" *ex* I.C.I.) and 25% chopped glass fibres (by weight) was moulded into rod using a melt extrusion process.

The initial billet machined from the moulded rod had a diameter of 9.8 mm, one end of which was machined to give an essentially conical nose of 5° semi-angle which was extended as a rod of 4mm diameter for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 110°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at an initial speed of 5mm min^{-1}. After 100mm of material had been drawn through the die, the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 69kg. The draw speed was then increased to a steady state value of 50mm min^{-1}. An oriented composite rod of actual deformation ratio 11 and a flexural Young's modulus of 14 GPa was obtained.

Example 12

A polyvinylidene fluoride homopolymer of $\bar{M}_w$ 351,200, $\bar{M}_n$ 171,000 (Solef XION, *ex* Solvay) was injection moulded using a mould with a 10mm diameter cylindrical cavity. The barrel temperature was 220°C and the mould temperature was 20°C. The mould was held under injection pressure for 5 minutes during which time it was cooled by progressive immersion in a water bath. This procedure ensured that solidification of the polymer took place from the bottom of the mould upwards, preventing the formation of internal voids due to shrinkage.

The initial isotropic billet was machined to a diameter of 9.80mm, one end being further machined to give an essentially conical nose of 5° semi-angle, which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and at a temperature 140°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 140°C, and was drawn through the die at a speed of 10mm min^{-1}. After 100mm of material had been drawn through the die, the drawing was stopped and the product was cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped, and drawing was recommeced at 10mm min^{-1}. The load rose to a value of 112 kg and remained constant thereafter.

An oriented rod of actual deformation ratio 6.00 and a flexural Young's modulus of 3.96 GPa was obtained.

In the case of polyvinylidene fluoride molecular weight restrictions are not found to be particularly critical. Desirably, however, the polyvinylidene fluoride has a number average molecular weight

from 1.0 to 1.9×10^5, preferably from 1.3 to 1.8×10^5, and a weight average molecular weight from 2×10^5 to 8×10^5.

Such material may be die-drawn to deformation ratios in excess of 6, for example 6.5 to 8 or even more.

Example 13

A high density polyethylene homopolymer of $\bar{M}_w$ 67,800, $\bar{M}_n$ 13,350 (140—60 *ex* BP Chemicals) was extrusion moulded into a cylindrical tube, which was then placed vertically in an oven to allow slow cooling solidification of the polymer.

An isotropic billet for die-drawing was machined to a diameter of 8.94mm one end being a cone of 5° semi-angle which was extended as a rod of 4mm diameter for gripping purposes.

The machined billet was advanced into a conical die of 15° semi-angle and bore diameter of 4mm, set at temperature of 110°C.

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at a preliminary draw speed of 5mm min^{-1}. After a length of material had been drawn through the die the process was stopped and the product was cut off at a short distance from the die. The oriented material protruding from the exit side of the die was then regripped and drawing continued. The haul-off speed was increased to 30mm min^{-1} whereupon the load rose to a steady value of 15 kg.

An oriented rod of actual deformation ratio 23.4 and a flexural Young's modulus of 45.4 GPa was obtained.

Example 14

A copolymer of ethylene and hex-1-ene (002—55 *ex* BP Chemicals was extrusion moulded in the following manner:

A melt extruder was used to fill a cylindrical aluminium mould, which was then placed vertically in an oven at 120°C to allow solidification of the polymer.

The initial, isotropic billet had a diameter of 11.31mm and one end was machined to give a conical nose of 5° semi-angle which was extended as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding nose of the billet was gripped at the exit side of the die and then the billet, at an initial temperature of 100°C was drawn through the die at a preliminary draw speed of 5mm min^{-1}. After a length of material had been drawn through the die the process was stopped and the product was cut off at a short distance from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 65 kg as the draw speed was gradually increased to steady state value of 100mm min^{-1}.

An oriented rod of actual deformation ratio 11.5 and a flexural Young's modulus of 15.2 GPa was obtained.

Claims

1. A process for the solid phase deformation of a workpiece of an orientable, thermoplastic polymer, which process comprises: providing the workpiece of the essentially unoriented polymer at the entry side of a die; applying to the workpiece from the exit side of a die a draw tension insufficient to cause tensile failure of the workpiece; and drawing the workpiece through the die so that its plastic strain is progressively increased during start-up of the process.

2. A process according to Claim 1 wherein the polymer is a semi-crystalline polymer.

3. A process according to Claim 2 wherein the polymer is an unsubstituted or fluoro-substituted vinyl polymer or a polyacetal.

4. A process according to Claim 3 wherein the polymer is a linear homo or copolymer of ethylene or propylene with at least one comonomer.

5. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of ethylene of $\bar{M}_w$ from 50,000 to 500,000.

6. A process according to Claim 5 where the die temperature is from 60°C below to below the melting point of the polymer.

7. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of propylene of $\bar{M}_w$ from 150,000 to 800,00.

8. A process according to Claim 7 wherein the die temperature is from 20°C to 170°C.

9. A process according to Claim 3 wherein the polymer is a polyoxymethylene.

10. A process according to Claim 9 wherein the die temperature is from 80°C to 170°C.

11. A process according to Claim 3 wherein the polymer is a vinylidene fluoride polymer.

12. A process according to Claim 11 wherein the die temperature is from 80°C to 165°C.

13. A process according to any preceding claim wherein the polymer is filled.

14. A process according to any preceding claim wherein that end of the workpiece to which the draw tension is applied is of progressively reduced cross section.

15. A process according to any preceding claim wherein the aperture of the die is progressively reduced during start-up of the process.

16. A process according to any preceding claim wherein the draw speed is at least 50cm min^{-1}.

17. A process according to any preceding claim which is continuous.

18. A process according to Claim 17 wherein the upstream end of a discrete workpiece being deformed in accordance with Claim 1 is welded to the downstream end of continuous stock of the same polymer and cross-section.

19. A process according to Claim 17 or 18

wherein the workpiece is continuously formed in situ.

20. A process according to any preceding claim where the workpiece is a filament, film or tube.

21. A process according to any preceding claim wherein the deformation ratio is greater than 10.

22. An oriented thermoplastic polymer whenever prepared by the process of any preceding claim.

23. A homo- or copolymer of propylene which has been deformed by a passage through a die in the solid phase and having a Young's modulus greater than 18 GPa.

24. A homo- or copolyoxymethylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 25 GPa.

25. A vinylidene fluoride polymer which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 3 GPa.

26. A copolymer of ethylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 10 GPa.

27. A copolymer according to Claim 26 having a Young's modulus greater than 30 GPa.

28. A copolymer of ethylene which has a Young's modulus greater than 40 GPa.

29. A copolymer according to any of Claims 26 to 28 wherein the comonomer comprises up to 5% of hexene-1.

30. A Portland cement, concrete or thermoset mass into which fibres according to any of Claims 22, 23 and 26 to 29 have been introduced.

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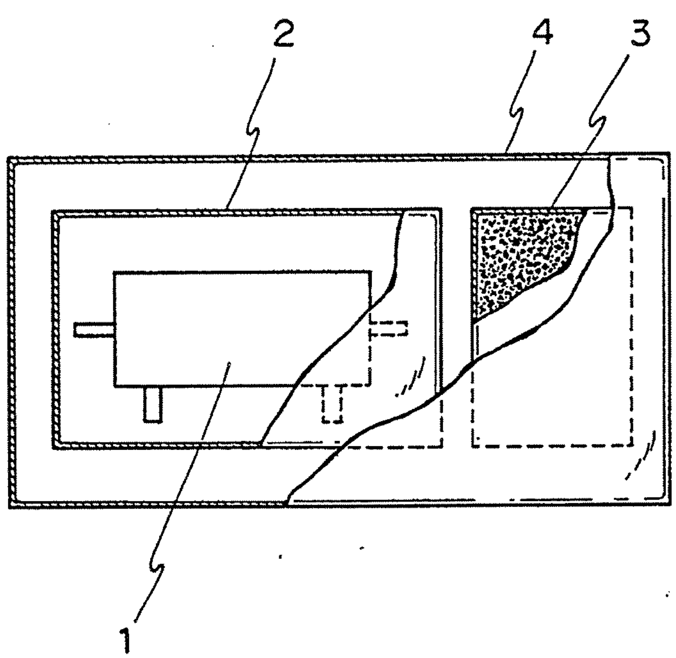
(54) Radiation-sterilized, packaged medical device

(57) A medical device package comprises a medical device 1; a gas-permeable sterile bag 2 containing the medical device 1 therein; a wrapping member 4 made of oxygen-impermeable material wherein said medical device-containing bag 2, previously subjected to radiation-sterilization, is sealed; and a deoxidizing agent 3 contained in the wrapping member 4 together with the medical device-containing bag 2.



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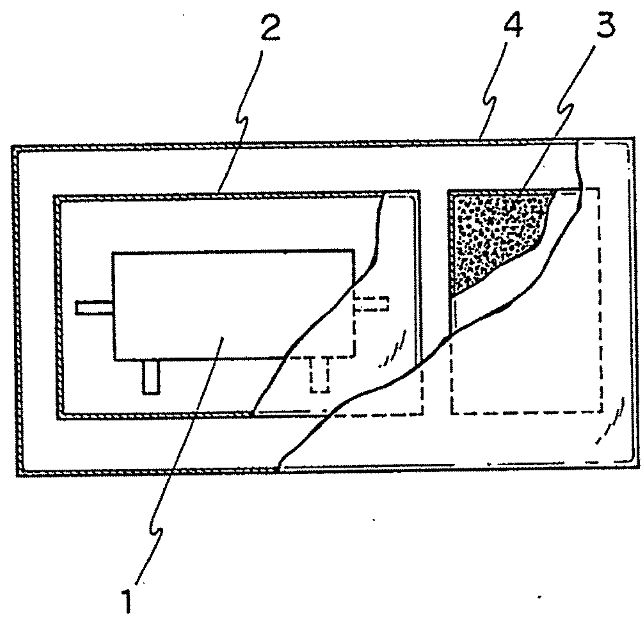
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SPECIFICATION

Radiation-sterilized, packaged medical device

The present invention relates to a radiation-sterilized medical device. More particularly, the present invention relates to a packaged medical device provided with a deodorizing means adapted to prevent emanation of an odor upon withdrawal of a radiation-sterilized medical device from a sterile containment bag.

As a method for sterilizing medical devices, sterilization with gamma-rays has been widely employed in recent years, particularly in the field of disposable medical devices. In order to maintain ster"ity up till the time of use, such a disposable medical device is generally sealed in a sterile bag and then sterilized with gamma-rays as pre-packaged in the bag. However, because of the presence of oxygen in the bag, irradiation with gamma-rays or other radiation excites the oxygen to yield ozone, an allotrope of oxygen, and, hence, generates the so-called gamma odor which is considered to be associated with ozone. This odor emanating upon unsealing of the sterile bag for removal of the medical device therefrom gives an uncomfortable sensation to the user of the device.

Furthermore, disposable medical devices are made, for the most part, of some plastic material or other and may suffer from decreased strength due to oxidation with time. Particularly in dry radiation-sterilization in a gaseous atmosphere where the surface of the plastic material is exposed to air, the presence of radiation-excited oxygen promotes oxidation of the plastic material with time at elevated temperature so as to induce a decrease in strength.

In view of the problems mentioned hereinbefore, the present inventors conducted an intensive research and discovered that these problems all spring out from the presence of oxygen. Accordingly, they sought for means for elimination of oxygen.

The object of the present invention is to provide a dry radiation-sterilized medical equipment which does not give off an odor upon unsealing and is free from decreases in the strength of plastic parts thereof.

This and other objects of the invention will become apparent from the description hereinafter.

The present invention provides a packaged medical device comprising a medical device; a gas-permeable sterile bag containing the medical device therein; a wrapping member made of oxygen-impermeable material and wherein said madical device-containing bag, previously subjected to radiation-sterilization, is sealed; and deoxidizing agent contained in the wrapping member together with the medical device-containing bag.

A schematic illustration of a packaged medical device in accordance with the present invention is shown on the accompanying drawing.

In the present invention, the radiation-sterilization is preferably sterilization with gamma-rays and the deoxidizing agent is preferably one based on activated iron oxide. The medical device to which the present invention can be applied with advantage includes a hollow fiber blood processing device, particularly a blood processing device employing a cellulose acetate hollow fiber membrane, which is generally believed to be incompatible with dry radiation-sterilization. The oxygen-impermeable material is preferably a laminated polyester-aluminum-polyethylene sheet.

According to the present invention, a medical device sealed in a sterile bag, after radiation-sterilization, is hermetically sealed in a wrapping member of oxygen-impermeable material together with a deoxidizing agent. For the reason, there is substantially no infiltration of oxygen from external environments and even the oxygen trapped in the course of the wrapping step is absorbed by the co-existing deoxidizing agent. Therefore, the inside of the wrapping member can be maintained in anoxic state so that the emanation of an odor and aging of the strength of the medical device can be successfully prevented.

Furthermore, since the sterile bag is a gas-permeable sterile bag, the oxygen and ozone present in the bag and the oxygen gradually released from the medical device are also instantly absorbed.

In addition, since the wrapping member is made of an oxygen-impermeable material, the entry of oxygen from the external environment is prevented almost completely and, therefore, an oxygen-free condition within the wrapping member can be maintained for a long time period.

An preferred embodiment of the present invention will now be described with reference to the accompanying drawing.

Referring to the drawing, a packaged medical device according to the present invention comprises a medical device 1 such as hollow fiber blood processing device, as sealed in a sterile bag 2 and further hermetically sealed, together with a deoxidizing agent 3, in a wrapping member 4. That is, the medical device 1 as such is first sealed in the sterile bag 2 and, then, after sterilization with gamma-rays, hermetically sealed into the wrapping member 4 together with the deoxidizing agent 3.

The sterile bag 2 is a gas-permeable sterile bag and the wrapping member 4 is made of an oxygen-impermeable material. The reason for using such a gas-permeable bag as the sterile bag

is that if a gas-impermeable sterile bag be employed, even if sealing is made under oxygen-free conditions, the oxygen inherent in the medical device itself is gradually released and collects within the sterile bag and, as experience tells, the decrease in strength of the medical device is accelerated at elevated temperature.

In the invention, the term "sterile bag" is intended to mean a bag which is subjected to sterilization treatment in a state that a medical device is contained therein and through the wall of which bacteria cannot pass. The sterile bag may be gas-permeable over the entire surfaces thereof or in a part thereof.

Examples of the sterile bag include the followings: (1) A bag, both sides of which are made of a laminated polyester-polyethylene film and which has one or more gas-permeable parts where one or more openings such as slit are provided in the laminated film and the opening portions are covered with a polyethylene non-woven fabric or a wood-free paper. (2) A bag, one side of which is made of a wood-free paper or a polyethylene non-woven fabric, and the other side of which is made of a laminated polyester-polyethylene film. (3) A bag, both sides of which are made of a wood-free paper or a polyethylene non-woven fabric.

The reason for using a wrapping member made of an oxygen-impermeable material is to prevent infiltration of oxygen from external environments and, hence, to ensure a long efficacy life of the deoxidizing agent. Examples of the wrapping member used in the invention include a laminated sheet consisting of an exterior polyester film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, a laminated sheet consisting of an exterior polyester film, an intermediate polyethylene film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, a laminated sheet consisting of an exterior biaxially orientated polypropylene film, an intermediate ethylene-vinyl alcohol copolymer film and an inner polyethylene film, a laminated sheet consisting of an exterior vinylon film having a polyvinylidene chlorine coating on both sides thereof and an inner polyethylene film, a laminated sheet consisting of an exterior biaxially orientated polyvinyl alcohol film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated orientated polypropylene film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated polyester film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated oriented nylon film and an inner polyethylene film, a laminated sheet consisting of an exterior polyvinylidene chloride-coated cellophane and an inner polyethylene film, and a laminated sheet consisting of an exterior laminated high impact polystyrene-polyvinlidene chloride-polyethylene film and an inner non-oriented polypropylene film. From the standpoint of cost and efficiency, the most preferred examples of the oxygen-impermeable material are a laminated sheet consisting of an exterior polyester film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film, and a laminated sheet consisting of an exterior polyester film, an intermediate polyethylene film, an intermediate aluminum foil (or aluminum deposition layer) and an inner polyethylene film.

The sterilization method may be any radiation-sterilization method, including one using gamma-rays and one utilizing electron beams. However, the present invention is more effective in case of sterilization with gamma-rays, which has a greater influence on the strength of the medical device, since the effect of the present invention which comprises sealing a medical device in an oxygen-impermeable wrapping member together with a deoxidizing agent is noticeably exhibited, especially when the problem of decreased strength of the medical device due to radiation-excited oxygen is taken into consideration.

The absorbed dose used in the radiation-sterilization varies depending upon the kind of medical device and the kind of radiation. In the case of sterilization of hollow fiber blood processing device with gamma-rays, an absorbed dose of 1.8 to 2.5 Mrad is usually used.

Because the deoxidizing agent is sealed together with a medical device contained in a gas-permeable sterile bag, it must be non-toxic. Moreover, the deoxidizing agent is preferably one which does not give rise to gases (hydrogen gas, carbon dioxide gas, and the like) upon absorption of oxygen. For these reasons, the deoxidizing agent is desirably one based on an active metal or metal compound and having its reaction rate, etc. controlled by a catalyst. The active metal or metal compound may for example be iron, zinc, copper or tin, or oxides of the foregoing metal but among the currently available deoxidizing agents, those based on activated iron oxide are most desirable. Among commercial deoxidizing agents of this type is Ageless (a commercial name of Mitsubishi Gas Chemical Company, Inc.). The deoxidizing agent is contained in a gas-permeable bag or container.

In the present invention, it is essential that, the medical device-containing bag is previously sterilized and then sealed together with a deoxidizing agent in an oxygen-impermeable wrapping member. That is, it must be avoided that a medical device is sealed together with a deoxidizing agent in a gas-impermeable bag and is subjected to radiation-sterilization in a state that the deoxidizing agent is present in the bag. The reason therefor is that when the medical device-containing bag is subjected to radiation sterilization in a state that a deoxidizing agent is present in the bag, the D value (which means the absorbed dose in which the number of bacteria is

reduced to one-tenth time that before irradiation) is increased. This tendency is marked particularly in the case of a medical device using cellulose acetate hollow fiber, as shown in Example 4. The tendency is also observed in the case of a medical device using silicone rubber hollow fiber.

As a method for removing the odor generated within the sterile bag, it might be contemplated to seal active carbon as a deodorant together with the medical device but in view of the fact that this material occupies more than 10 times the volume of a typical deoxidizing agent, that its deodorizing efficiency is poor at elevated temperature, and that it does not prevent the decrease of strength with time, for instance, the use of active carbon is not suitable for the purposes of the present invention.

Referring to the medical device to be packed according to the present invention, the method for inhibiting decrease of strength in accordance with the present invention, that is a method comprising sealing a medical device contained in a gas-permeable sterile bag in an oxygen-impermeable wrapping member together with a deoxidizing agent after radiation-sterilization, can be applied to the radiation-sterilization of any medical device basically made of a plastic material. For example, the present invention is of course effective for a medical device such that its loss of strength will be confined within a tolerable range even without provision of any specific means for preventing such decrease of strength. However, from the standpoint of cost and efficiency, the present invention can be preferably applied to hollow fiber blood processing devices, particularly to blood processing devices employing cellulose acetate hollow fiber membranes. Typical example of hollow fiber blood processing devices includes dialyzer for artificial kidney. The present invention is also preferably applied to artificial lung employing silicone rubber hollow fiber membranes and catheter made of silicone rubber.

The present invention is more specifically described and explained by means of the following Examples. It is to be understood that the present invention is not limited to the Examples, and various change and modifications may be made in the invention without departing from the spirit and scope thereof.

Example 1

A dialyzer containing a bundle of 8,800 cellulose acetate hollow fibers each having an effective length of 20 cm, an outer diameter of 230 μm and an inner diameter of 200 μm was placed in a gas-permeable sterile bag, both sides of which was made of a laminated polyester-polyethylene film and which had a slit on the one side thereof with the slit portion being covered with a polyethylene non-woven fabric, and the bag was sealed. The bag containing the dialyzer was sterilized by irradiation of gamma-rays in a dose of 2.5 Mrad. The sterilized bag was inserted together with 10 g of Ageless as a deoxidizing agent into a wrapping member in the form of bag and made from a laminated sheet consisting of a polyester film having a thickness of 12 μm, an aluminum foil having a thickness of 9 μm and a polyethylene film having a thickness of 40 μm, which layers were laminated in that order, and the wrapping member was heat-sealed.

The deodorizing effect was determined at appropriate time intervals. The results are shown in Table 1. In Table 1, 1W, 2W and 4W represent the storage periods of 1, 2 and 4 weeks, respectively. The symbols in Table 1 mean the followings:

○ : No odor is detected.
× : Odoe is detected.

Example 2

The same procedures as in Example 1 were repeated except that a laminated sheet consisting of a polyester film having a thickness of 12 μm, a polyethylene film having a thickness of 15 μm, an aluminum foil having a thickness of 9 μm and a polyethylene film having a thickness of 40 μm, which layers were laminated in that order, was used as a wrapping member.

The results are shown in Table 1.

Comparative Examples 1 and 2

The same procedures as in Example 1 were repeated except that 50 g of an active carbon was used instead of Ageless (Comparative Example 1) or both Ageless and the active carbon were not used (Comparative Example 2).

The results are shown in Table 1.

Table 1

Storage condition		Blank (no irradiation)	Irradiation (2.5 Mrad)			
Temp. (°C)	period		Ex. 1	Ex. 2	Com. Ex. 1	Com. Ex. 2
40	1 W	○	○	○	○	×
	2 W	○	○	○	○	×
	4 W	○	○	○	×	×
50	1 W	○	○	○	○	×
	2 W	○	○	○	×	×
	4 W	○	○	○	×	×
60	1 W	○	○	○	×	×
	2 W	○	○	○	×	×
	4 W	○	○	○	×	×

The results of Table 1 reveal that the use of a deoxidizing agent produces a noticeable deodorizing effect.

Example 3

The same hollow fiber as used in Example 1 was sterilized and packaged in the same manner as in Example 1. The aging of the strength of the follow fiber was determined. The results are shown in Table 2. In Table 2, each strength value is expressed in terms of an average value ± standard deviation for ten hollow fibers.

Comparative Example 3

The same procedures as in Example 3 were repeated except that no deoxidizing agent was used. The results are shown in Table 2.

Table 2

Storage condition		Blank (No irradiation)		Irradiation (2.5 Mrad)			
				Ex. 3		Com. Ex. 3	
Temp. (^{o}C)	Period	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)	Tensile strength at breaking (g/fiber)	Elongation at breaking (%)
40	1 W	76 ± 13	80 ± 11	76 ± 10	82 ± 13	75 ± 6	81 ± 12
	2 W	78 ± 10	81 ± 10	77 ± 8	79 ± 8	61 ± 8	73 ± 10
	4 W	77 ± 11	79 ± 12	77 ± 10	80 ± 10	55 ± 7	72 ± 14
50	1 W	78 ± 12	80 ± 10	77 ± 8	80 ± 12	70 ± 5	75 ± 8
	2 W	77 ± 11	79 ± 13	78 ± 6	81 ± 10	58 ± 7	72 ± 13
	4 W	79 ± 10	79 ± 7	76 ± 10	79 ± 12	49 ± 8	70 ± 10
60	1 W	78 ± 12	80 ± 10	76 ± 12	79 ± 9	58 ± 7	73 ± 8
	2 W	76 ± 10	80 ± 6	76 ± 8	80 ± 12	42 ± 5	67 ± 10
	4 W	77 ± 15	79 ± 11	75 ± 10	79 ± 8	31 ± 6	50 ± 12

The results of Table 2 reveal that the use of a deoxidizing agent contributes remarkably to prevention of decrease in strength due to aging from the hollow fiber.

Example 4

The same dialyzer as used in Example 1 was placed in the same sterile bag as used in the Example 1 and gamma-rays were irradiated thereto. The D value was determined with respect to Bacillus pumilus ATCC 27142. The results are shown in Table 3.

The same procedures as in the above were repeated with a dialyzer using polypropylene hollow fibers or an artificial lung using silicone rubber hollow fibers. The results are also shown in Table 3.

Comparative Example 4

The same procedures as in Example 4 were repeated except that each medical device was placed together with Ageless in the same oxygen-impermeable wrapping member as used in Example 1 and then subjected to irradiation of gamma-rays. The results are shown in Table 3.

Table 3

Hollow fiber	D value (Mrad)	
	Ex. 4	Com. Ex. 4
Cellulose acetate	0.213	0.405
Polypropylene	0.197	0.210
Silicone rubber	0.167	0.258

Results of Table 3 reveal that the irradiation of gamma-rays in the presence of a dioxidizing agent invites a great increase in the D value, particularly in the case of cellulose acetate hollow fiber. Therefore, it is desirable that the irradiation of gamma-rays is carried out in the absence of a dioxidizing agent.

In addition to the elements and ingredients used in the Examples, other elements and ingredients can be used in the Examples as set forth in the specification to obtain substantially the same results.

It will be apparent from the foregoing description that since the present invention comprises sealing a medical device contained in a gas-permeable sterile bag further in an oxygen-impermeable wrapping member together with a deoxidizing agent, it eliminates the oxygen from the wrapping member as well as from the sterile bag and even disposes of the oxygen emanating gradually from the medical device as well.

Furthermore, since the wrapping member is made of an oxygen-impermeable material, there is substantially no entry of external oxygen so that the deoxidizing agent may retain its function for an extended time period.

CLAIMS

1. A packaged medical device comprising a medical device; a gas-permeable sterile bag containing the medical device therein; a wrapping member made of oxygen-impermeable material and wherein said madical device-containing bag, previously subjected to radiation-sterilization, is sealed; and a deoxidizing agent contained in the wrapping member together with the medical device-containing bag.

2. The packaged medical device of Claim 1, wherein said radiation sterilization is dry radiation-sterilization in a gaseous atomosphere.

3. The packaged medical device of Claim 2, wherein said dry radiation-sterilization is sterilization with gamma-rays.

4. The packaged medical device of Claim 1, wherein said deoxidizing agent is based on activated iron oxide.

5. The packaged medical device of Claim 1, wherein said medical device is a hollow fiber blood processing device.

6. The packaged medical device of Claim 5, wherein said hollow fiber blood processing device is a dialyzer using a cellulose acetate hollow fiber membrane.

7. The packaged medical device of Claim 5, wherein said hollow fiber blood processing device is an artificial lung using a silicone rubber hollow fiber membrane.

8. The packaged medical device of Claim 1, wherein said oxygen-impermeable wrapping

member is a laminated polyester-aluminum-polyethylene sheet.

9. The packaged medical device of Claim 1, wherein said oxygen-impermeable wrapping member is a laminated polyester-polyethylene-aluminum-polyethylene sheet.

10. A packaged medical device as claimed in claim 1, substantially as described herein with reference to the accompanying drawing.

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(58) Field of search
B5A

(54) Die drawing of tubular thermoplastics

(57) A hollow workpiece (9) comprising an orientable, thermoplastic polymer is drawn down in sectional area by passage in the solid phase through a die (7) having both an entry side and an exit side, by applying to the hollow workpiece (9) from the exit side of the die a tension insufficient to cause tensile failure of the workpiece but sufficient to deform the hollow workpiece by drawing it with reduction in its bulk cross-sectional area in the solid phase simultaneously thriugh the die (7) and over an internally positioned former (4, 3, 5,) having a cross-sectional area greater than the initial internal cross-sectional area of the hollow workpiece; and collecting the deformed hollow workpiece (10) from the exit side of the die.

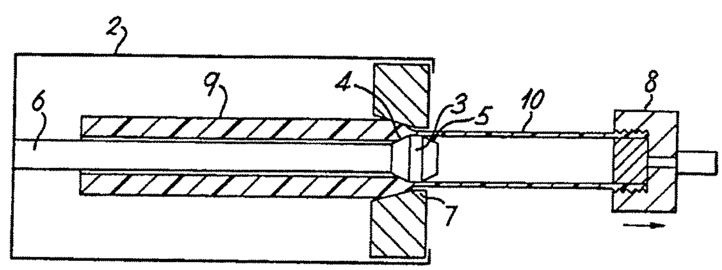

Fig. 1

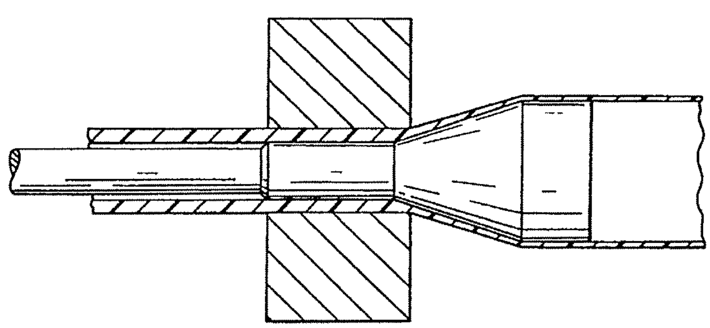

Fig. 5

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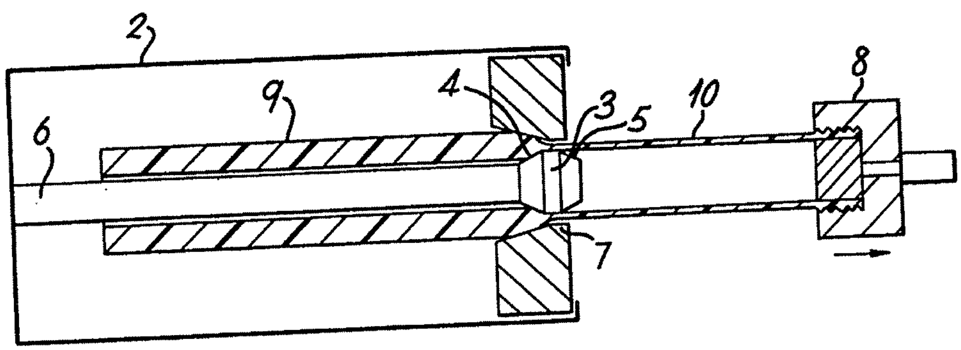

Fig. 1

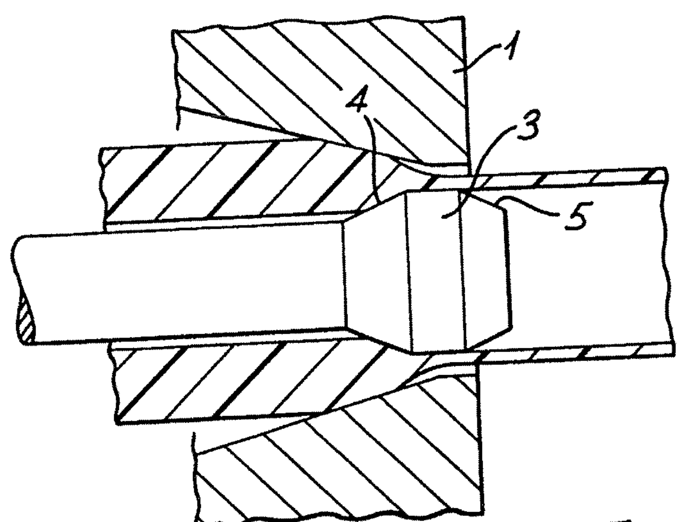

Fig. 2

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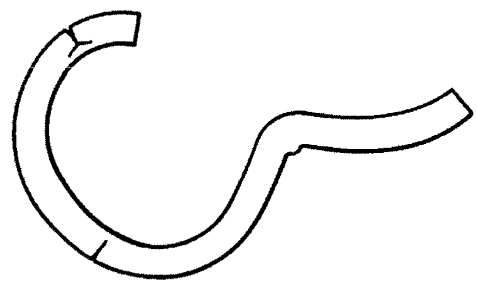

Fig. 3

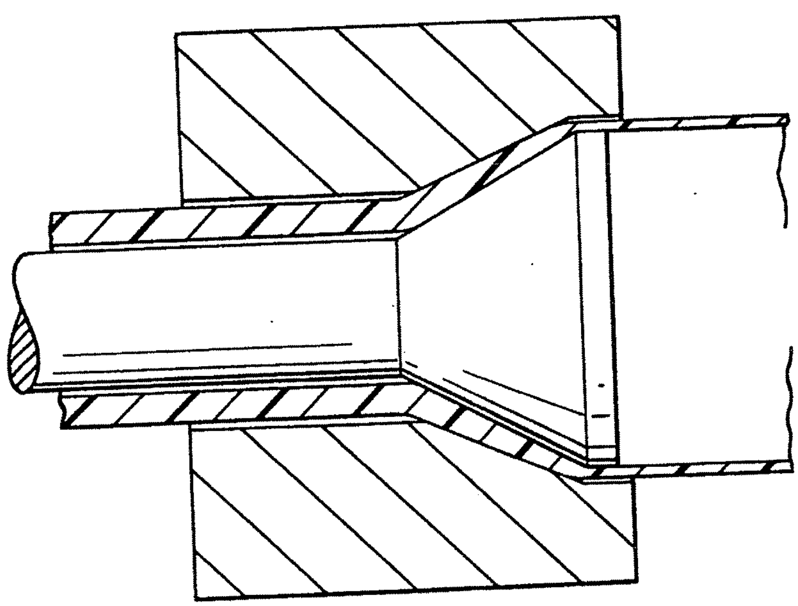

Fig. 4

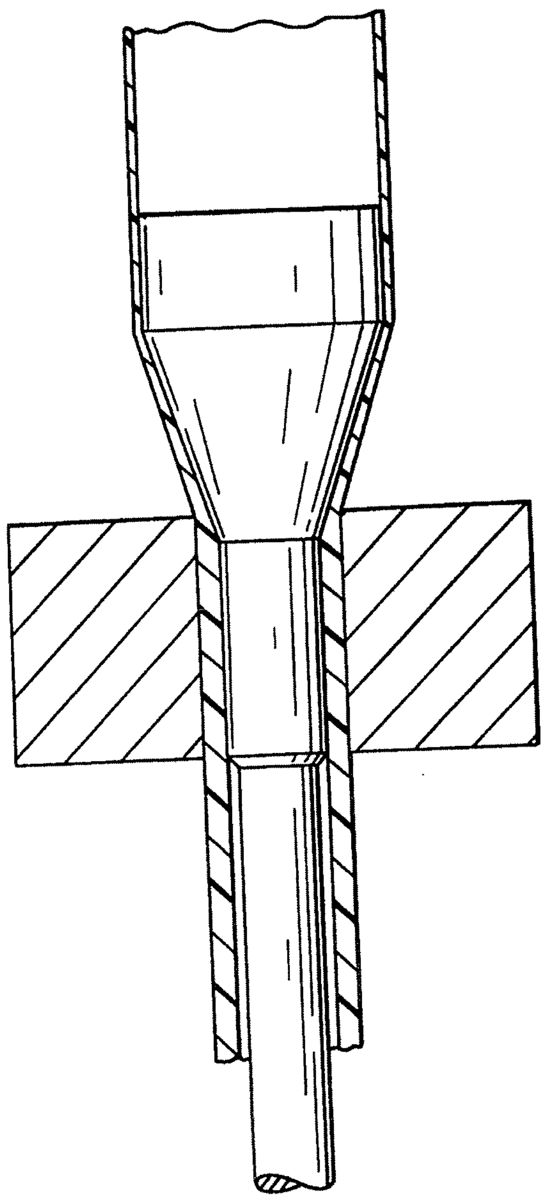

Fig. 5

SPECIFICATION

Tubular materials

This invention relates to tubular materials; more particularly, this invention relates to a process for the solid phase deformation of tubular materials of an orientable, thermoplastic polymer and to the oriented tubular materials so produced.

In our patent GB 2060469B we have described a process for the solid phase deformation of a workpiece of an orientable, thermoplastic polymer, which process comprises providing the workpiece of the essentially unoriented polymer at the entry side of a die; applying to the workpiece from the exit side of the die a draw tension insufficient to cause tensile failure of the workpiece; and drawing the workpiece through the die so that its plastic strain is progressively increased during start-up of the process.

This invention seeks to provide oriented tubular materials having improved mechanical properties, especially in directions other than the machine direction.

According to the present invention, there is provided a process for the deformation of a hollow workpiece comprising an orientable, thermoplastic polymer by passage in the solid phase through a die having both an entry side and an exit side, which process comprises providing the hollow workpiece at the entry side of the die; applying to the hollow workpiece from the exit side of the die a tension insufficient to cause tensile failure of the workpiece but sufficient to deform the hollow workpiece by drawing it with reduction in its bulk cross-sectional area in the solid phase simultaneously through the die and over an internally positioned former having a cross-sectional area greater than the initial internal cross-sectional area of the hollow workpiece; and collecting the deformed hollow workpiece from the exit side of the die.

By "bulk cross-sectional area" of the hollow workpiece is meant the area of the bulk of the workpiece substantially normal to the machine direction; by "internal cross-sectional area" of the hollow workpiece is meant the area of the hollow within the workpiece substantially normal to the machine direction. By way of example, in a tubular workpiece, the former area is $\pi_4(D_o^2-D_B^2)$ where D_o is the outside diameter and D_B is the bore of the tubular workpiece while the other area is $\pi_4 D_B^2$.

The process of the present invention is effected by utilising at the die and, optionally, downstream therefrom a former internally positioned within the hollow workpiece and having a cross-sectional area of at least the initial internal cross-sectional area of the hollow workpiece and, preferably, the same cross-section. Preferably the cross-sectional area of the former is greater than the initial internal cross-sectional area of the hollow workpiece and this may advantageously be provided by a former of progressively increasing cross-sectional area.

The term "hollow workpiece" as used herein includes tubes and other cross-sections of hollow stock. The term includes both billets and other forms of stock of greater length; indeed, continuous stock, which may be formed as the process is performed, may be utilised. Examples include open-ended elongate workpieces of substantially constant cross-section, desirably with an axis of symmetry; for example, hollow workpieces of circular, elliptical, square, rectangular or triangular cross-section.

The orientable thermoplastic polymer desirably is or becomes a semicrystalline polymer, especially one which exhibits sufficient strain hardening and strain rate dependence of the flow stress to stabilise the neck formed under the desired drawing conditions. Preferred classes of such polymers are unsubstituted or mono- or poly- halo-, for example chloro- or fluoro-substituted vinyl polymers, unsubstituted or hydroxy-substituted polyesters, polyamides, polyetherketones and polyacetals. Suitable examples include a linear homo- or copolymer of ethylene or propylene with at least one comonomer; a vinyl chloride polymer, a vinyl fluoride polymer or a vinylidene fluoride polymer; PHB; PEEK; or a homo- or co-polyoxymethylene.

The polyester is one which is derivable from the reaction of at least one polyhydric alcohol, suitably a linear polyhydric alcohol, preferably a diol, with at least one polybasic acid, suitably a polycarboxylic acid. The alcohol is preferably an alicyclic or aliphatic such alcohol; for example, cyclohexanedimethanol or a linear C_2 to C_6 alkylene diol such as ethylene glycol, 1,3-propylene glycol or 1,4-butylene glycol, especially ethylene glycol. The acid is preferably an aromatic, alicyclic or aliphatic such acid; for example a mono- or poly carbocyclic aromatic acid such as *o*, m-, or terephthalic acid; 2,6- or 1,5-naphthalene dicarboxylic acid; or 1,2-dihydroxybenzoic acid, especially terephthalic acid. Examples of suitable polyesters include polyethylene 2,6-naphthalate, polyethylene 1,5-naphthalate, polytetramethylene 1,2-dihydroxybenzoate, polyethylene terephthalate, polybutylene terephthalate and copolyesters, especially of ethylene terephthalate.

Where it is intended to utilise the die drawing process of this invention to produce a product with enhanced Young's modulus; resistance to creep; resistance to gas transport; enhanced deadfold; or enhanced axial thermal conductivity then a workpiece of a linear homo- or copolymer of ethylene should desirably comprise a polymer having a weight average molecular

weight ($\overline{M}_w$) less than 1,000,000, suitably from 50,000 to 500,000, preferably from 70,000 to 400,000; one of a linear homo- or copolymer of propylene should desirably comprise a polymer having a $\overline{M}_w$ from 150,000 to 800,000, preferably from 250,000 to 500,000.

However, the die drawing process of this invention may also be performed, to provide a more advantageous forming process but not the enhanced properties listed above, on a hollow workpiece of an orientable, amorphous polymer: for example polymethyl methacrylate or polystyrene; or of an orientable, semicrystalline ultra high molecular weight polymer (for example, a linear homopolymer of ethylene having a $\overline{M}_w$ about 3,000,000). It may likewise be utilised, but to a lower deformation ratio, in respect of those polymers which would otherwise give the enhanced properties lised above.

The hollow workpieces used in the process of this invention may incorporate a filler. Examples of useful fibrous fillers include glass, asbestos, metal, carbon and ceramic whiskers, such as those formed from silicon carbide. Examples of useful laminar fillers include mica, talc and graphite flakes. Chalk and fly ash may also be included. The amount of filler which may advantageously be included depends on the nature of the filler, but up to 50% by weight, preferably less than 30%, especially less than 20%, may be incorporated.

The hollow workpiece may be essentially unoriented before deformation. The term "essentially unoriented" as used herein means that the hollow workpiece has incurred no orientation other than that minor amount which might be induced during formation of the workpiece, (including orientation produced in the semi-molten state) for example during billet moulding or melt extrusion, or during any subsequent shaping thereof, for example by machining, prior to the performance of the die drawing process of this invention.

Where it is not possible to use the polymer as received as a hollow workpiece, the workpiece may be formed either in the batch or continuously. In either case care must be taken to ensure that the workpiece cools at an appropriate rate so that the resulting hollow workpiece will be without defects.

In the case of a hollow workpiece formed in the batch, for example a polymer billet, the following general methods have been found to be suitable. The polymer may be melted in a screw extruder; extruded or injected into a billet mould at a temperature about 30°C above its melting point and cooled under elevated pressure for 5 hours, or it may be melted in an extruder; extruded or injected into a cold billet mould; transferred to an oven for 4 hours under ambient pressure at a temperature below its melting point but above its crystallisation temperature; and thereafter allowed to cool in the oven after the heating has been switched off. The polymer may also be injection moulded into an air or water cooled billet mould. Progressive immersion in the cooling fluid is preferred, thereby ensuring that solidification of the polymer takes place from the bottom of the mould thereby preventing the formation of internal voids due to shrinkage. The hollow workpiece may be formed in the batch by including a mandrel of appropriate cross-section, usually coaxially, in the mould. Alternatively, stock of circular or other hollow cross-section may be produced continuously using one of several processes known to those skilled in the art.

As the hollow workpiece is to be drawn over a former having a cross-sectional area greater than the internal cross-sectional area of the hollow workpiece a belled nose must first be formed on the hollow workpiece to permit start-up. This may be produced by rolling the hollow workpiece onto the former; inflating an elastomeric bag inside the nose region of the hollow workpiece; or drawing a conical former upstream into the nose region of the hollow workpiece.

In performance of the invention a nose formed on the hollow workpiece is advanted to protrude through the die lips and is secured to tensioning means applied from the exit side of the die. A suitable arrangement includes a hauloff comprising a pair of serrated jaws in which the nose is gripped; a high tensile cable one end of which cable is attached to the jaws, the other to a winch or a loading station to which a turning moment or mass may be applied thereby applying a draw tension to the nose. The hauloff may also comprise, instead of a cable, any tension transmitting means used in the metal drawing art including a chain, a rack and pinion mechanism, a screw mechanism and a hydraulically operated draw mechanism. The hauloff may further comprise a pair of continuous contra-rotating friction belts, generally known as a "caterpillar" ("CATERPILLAR" is a registered Trademark.)

The draw tension should be sufficient to draw the hollow workpiece through the die but insufficient to cause tensile failure of the article; that is, the draw tension should be such that the true stress at any point of the product does not exceed its fracture stress at that point. A suitable maximum value of draw tension may readily be determined by routine experiment. In the case of strain hardening polymers, as the drawing progresses the flow stress of the strained portions of the workpiece increases. This will permit a greater draw tension to be applied (giving an increased plastic strain). This enables greater cross-sections of workpiece, or smaller apertures of die, or both, to be utilised also giving a further increase in plastic strain. These increases further strengthen the strained polymer so that the strain can be progressively increased during start-up until a product having desired final properties (for example, Young's

modulus or cross-sectional area) is attained whereafter steady state processing conditions obtain.

After a grippable length of the hollow workpiece has been drawn through the die any unsuitably oriented part of its nose may be removed and the oriented grippable length re-gripped thereby enabling a higher load to be applied.

For a particular polymer, a steady state process is obtained for a given set of temperature, draw speed and deformation ratio. "Deformation ratio' as used herein is the ratio of the initial cross-sectional area of the hollow workpiece to the final cross-sectional area of the product. These parameters vary implicitly, but it has been found possible, for a particular polymer, to set the die temperature (which will be only a nominal temperature for the polymer since the process is not an isothermal one) and the workpiece shape and vary, by experiment, the draw speed to obtain the desired deformation ratio.

For linear homo- and copolymers of ethylene the hollow workpiece is desirably heated to a temperature within 60°C below the melting point of the polymer. More particularly, for such polymers of $\overline{M}_w$ from 50,000 to 150,000, the temperature is preferably from 70°C to 100°C; and for such polymers of $\overline{M}_w$ above 300,000 from 70°C to 120°C. For linear homo- and copolymers of polypropylene of weight average molecular weight from 150,000 to 800,000 the hollow workpiece is desirably heated to a temperature from 20°C to 170°C, preferably 90°C to 130°C. A temperature of 80°C to 170°C, preferably 150°C to 170°C is suitable for homo- or copolyoxymethylene; of 80°C to 165°C is suitable for vinylidene fluoride polymers and of 55°C to 110°C or even 55°C to 120°C is suitable for polyester. The polymer temperature may be further controlled by utilising a heated die and/or a temperature controlled chamber which extends downstream. Certain polymers may also be heated by subjecting them to a dielectric field, as disclosed in EPC 0084274 and US 3364294.

Very clear oriented, polyester material may be prepared by the process of the invention by heating an orientable thermoplastic workpiece of the polyester material to a temperature from 55°C to 105°C, preferably from 60°C to 90°C, at the entry side of the reducing die; and deforming the workpiece by passage through the die in the solid phase at a nominal deformation ratio of at least 2:1, preferably of at least 3:1.

If a measure of clarity may be sacrificed the workpiece may be heated above 105°C; for example to 110°C or even to 115°C above which temperature the resulting product is both cloudy and of diminished modulus.

It is feasible to use draw speeds greater than 1 cm min^{-1} in the die drawing process of this invention; indeed, speeds of 50 cm min^{-1} or more are preferred.

A batch process may be converted to a continuous one by putting the upstream end of the deforming hollow workpiece and the downstream end of stock of the same cross-sectional both in contact with a hot, stainless steel plate; removing the plate and welding the two polymer surfaces. Preferably such a weld should be at an angle of 45° or less to the axis of the stock.

Utilising the die drawing process of this invention on polymers which show adequate strain hardening and strain rate dependence of the flow stress, it is possible to obtain deformation ratios of at least 4, preferably 10 or even more.

Deformation ratios readily attainable by the process of this invention are 4:1 (PEEK); 4:1 to 6:1 (PET, PVDF and polyamide); 7:1 to 9:1 (POM); and 8:1 to 12:1 (polyolefins).

The invention will now be further described, by way of example, with reference to the accompanying drawings in which:

Figure 1 represents a schematic side elevation of the apparatus diametrically sectioned along the machine direction;

Figure 2 represents a detailed side elevation of the die geometry in which at least a portion of the die bore is convergent;

Figure 3 represents a hoop prepared and deformed as described in the Example;

Figure 4 represents a detailed side elevation of die geometry differing from that of Fig. 2 in that at least a portion of the die bore is divergent; and

Figure 5 represents a detailed side elevation of die geometry differing from that of Fig. 2 in that the die bore is constant.

It is observed that in each of the geometries illustrated in Figs. 2, 4 and 5 at least a portion of the die-former configuration defines a reducing cross-sectional area for the flow path of the deforming hollow workpiece.

In the drawing, the apparatus consists of a reducing die 1 of 15° semi-angle and maximum reduction (or ideal deformation) ratio of 2.68 and, upstream thereof, an oven 2 from which a mandrel 3 (21.8 mm diameter and 10 mm length), having tapered leading and trailing edges 4, 5, is supported by rod 6 (16 mm diameter) in the die exit 7 which is 1 cm in length and without taper. Hauloff jaws 8 are connected downstream from the reducing die to a winch (not shown).

In use, an initial hollow workpiece 9 of orientable thermoplastic polymer is machined at one end to form a nose. It is then inserted over the mandrel and rod into the oven, maintained at a temperature of 100°C, so that the machined end protrudes through the die exit, the die also

being maintained at 100°C. The machined end is next gripped in the hauloff jaws and load applied, slowly at first such that the plastic strain of the billet is progressively increased without causing tensile failure. After start-up a steady drawing speed at a steady drawing load is established.

The following Examples illustrate the invention.

EXAMPLE 1

An ethylene copolymer of the following specification:

0.7	$-CH=CH_2$ groups/1000 C atoms
1.4	$-CH_3$ groups/1000 C atoms
$\overline{M}_w$	205,500
$\overline{M}_n$	18,000
$\overline{M}_w\overline{M}_n$	11.4

(Marlex 47100 *ex* Phillips; "MARLEX" is a registered Trade Mark) was melt extruded into a billet mould having an internal diameter of 3 inches at 220°C; and cooled to ambient temperature under elevated pressure for 15 hours to give a void-free billet 700 mm in length.

This billet was then bored-out to 25 mm I.D. and machined externally to 63 mm O.D.; and a nose, 100 mm in length, was then machined on one end of the billet by continously increasing the bore to 40 mm and continously turning down the outer surface to 52 mm O.D., the two frusto-conical surfaces so generated each having a semivertical angle of 7°. The hollow billet so formed was next incorporated into the aforementioned apparatus and heated to 100°C.

After being left for at least 2 hours in the apparatus at the temperature of 100°C in order to attain thermal equilibrium, the protruding nose of the billet was gripped by a clamp at the exit side of the die and the billet, at an initial temperature of 100°C, was drawn through the die at a speed of 10 mm min^{-1} at a tension of about 400 kg wt until sufficient oriented polymer appeared to enable repositioning of the clamp whereupon this process was repeated until drawn material from the bulk of the billet appeared at the exit side of the die. After a final repositioning of the clamp drawing was recommenced at a draw speed of 190 mm min^{-1} at a tension of 1400 kg wt until substantially all of the billet has been drawn to given an oriented ethylene copolymer tube of 40.5 mm O.D. and 32.2. mm I.D. and having an actual deformation ratio of 5.5.

10 mm lengths were cut from the tube to provide hoops; it was found that they could be deformed in a vice in a direction at right angles to the machine direction to a substantial strain in which the vice jaws were only 24 mm apart before fracture of the hoops occured. Even on fracture the hoops remained intact, the cracks not having propagated to the internal surfaces of the hoops.

If a portion of a hoop is deformed instead by application of a net force away from the centre of curvature of the hoop the internal surface of the hoop does not fracture but, rather, undergoes plastic flow.

A more quantitative test is now described which was effected to demonstrate the enhanced ductility of the tubes produced in accordance with the present invention.

A soft rubber bung was inserted into a length of the tube prepared as aforesaid. The bung was then compressed by two pistons mounted to be contra-axially and internally slidable in the tube. A circumferential scale measured the maximum change in girth of the tube prior to rupture. The force applied to the pistons was a measure of the rupture stress generated.

It was found that the tube expanded in girth by 4.6% before breaking at a rupture stress of 30 MPa. A comparison tube of the same polymer prepared as disclosed in GB 2060469B expanded in girth by 1.3% before breaking at a rupture stress of 26 MPa. It will be seen, therefore, that the tube of the present invention exhibited a nearly threefold increase in ductility over the tube prepared as disclosed in GB 2060469B.

EXAMPLE 2

A length of clear tube of isotropic, amorphous polyethylene terephthalate of 18.5 mm I.D. and 25 mm O.D. (as received *ex* AKZO) was pre-treated, prior to drawing, in the following way. The tube was mounted as a bung to a high pressure air line. The central portion of the tube was then heated inside a mould by pouring water at 95°C thereover and, while hot, expanded by admitting air into the tube at 100 p.s.i. With the air pressure maintained the tube was quenched by immersion in a water bath at ambient temperature. The air pressure was next released and the bubble so formed was sawn through at its equator to provide two bell-ended tubular billets.

The billet so formed was then incorporated into the aforementioned apparatus in which the mandrel and die tooling was that shown in Fig. 4 of the accompanying drawings and wherein the frusto-conical portion of the mandrel has a 15° semi-angle expanding from a 18 mm

diameter to a 35 mm diameter while the die has a semi-angle of approximately 13°. The billet was heated to 75°C and maintained for 1 hour at that temperature in order to attain thermal equilibrium.

At low drawing speeds (typically 1 cm min^{-1}) noisy stick-slip occurred and the resulting tube had a irregular, rather thick (1.2 mm) wall of 36 mm O.D. However, with higher drawing speeds stick-slip disappeared: at a drawing speed of 30 cm min^{-1} a clear, smooth tube was produced with a 27 mm O.D. If the drawn product was quenched as it left the mandrel it was found that the tube retained a higher O.D; for example, at a drawing speed of 65 cm min^{-1} clear, smooth tube of 33 mm O.D. and a wall thickness of 0.5 mm was produced.

The drawn product was qualitatively assessed to be very tough and crease-proof. Further drawing of strips cut in the machine direction was not possible at ambient temperature. Circumferential strips could, however, be drawn by approximately 100%.

EXAMPLE 3

A length of unplasticised PVC thick walled tube of 32 mm I.D. and 42 mm O.D. (Polyorc BS 3505 CL7 *ex* ICI) was pre-treated, prior to drawing, in the following way.

A bell-end was formed at one end of the tube by pulling a metal taper-nosed cylinder of the following configuration: cylindrical nose 32 mm diameter, 30 mm long; then a cone of 15° SVA leading to a cylindrical body of 59 mm, 70 mm long, heated to 150°C, into it. The tube was originally at room temperature but the end to be deformed received heat from the hot cylinder. This softened the tube and allowed the tapered cylinder to be drawn into the tube along a length of 15 cm, thereby expanding the end. The tube was then cooled with the taper in place, after which the taper was removed. (The operation was made easier both by greasing the taper and also by chamfering the leading edge of the tube.)

The bell-ended billet so formed was next heated in an oven to 95°C and drawn through the mandrel and die tooling shown in Fig. 5 of the accompanying drawings and maintained at the same temperature.

The dimensions of the die were: Length 60 mm; Bore diameter 42 mm.

The dimensions of the mandrel were:

Cylindrical neck 32 mm diameter, 60 mm long;

Conical expanding zone 15° SVA leading to; a short cylindrical section 5 mm long, 58 mm diameter. The mandrel was fitted so that its neck was coaxially within the die and the conically expanded part was substantially outside the die and downstream therefrom but held in position so that a constriction was formed between the downstream end of the die and the upstream end of the expanding cone of the mandrel. The constriction reduced, the tube wall thickness at this point from 5.0 mm to 3.7 mm regulating and controlling the flow of the deforming PVC tube. The mandrel was provided with a hole for a cartridge heater. This heater brought the temperature of the mandrel to 95°C prior to start up, when it was removed. A soak time of 1–2 hours was allowed for the billet, oven and mandrel to attain equilibrium. The inside of the billet was lightly lubricated with grease.

The expanded end of the billet was then grasped and the billet drawn at a speed of 70 cm/min, the draw force being 350 kg.

The resulting product was a shiny uniform, tough tube 61 mm outside diameter; 55 mm bore diameter.

This corresponds to a hoopwise expansion of 1.6X and a lengthwise extension of 1.05X.

In accordance with a further aspect of this invention, a deformed hollow workpiece of this invention may be further fabricated, for example by slitting and/or rolling into sheet stock.

CLAIMS

1. A process for the deformation of a hollow workpiece comprising an orientable, thermoplastic polymer by passage in the solid phase through a die having both an entry side and an exit side, which process comprises providing the hollow workpiece at the entry side of the die; applying to the hollow workpiece from the exit side of the die a tension insufficient to cause tensile failure of the workpiece but sufficient to deform the hollow workpiece by drawing it with reduction in its bulk cross-sectional area in the solid phase simultaneously through the die and over an internally positioned former having a cross-sectional area greater than the initial internal cross-sectional area of the hollow workpiece; and collecting the deformed hollow workpiece from the exit side of the die.

2. A process according to Claim 1 wherein the polymer comprising the hollow workpiece is a semicrystalline polymer.

3. A process according to Claim 2 wherein the polymer is an unsubstituted or mono- or poly halo-substituted vinyl polymer, unsubstituted or hydroxy-substituted polyester, a polyamide or a polyacetal.

4. A process according to Claim 3 wherein the polymer is a linear homo-or copolymer of ethylene or propylene with at least on comonomer.

5. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of ethylene of $\overline{M}_w$ from 50,000 to 500,000.

6. A process according to Claim 5 wherein the hollow workpiece is heated to a temperature within 60°C below the melting point of the polymer.

7. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of propylene of $\overline{M}_w$ from 150,000 to 800,000.

8. A process according to Claim 7 wherein the hollow workpiece is heated to a temperature from 20°C to 170°C.

9. A process according to Claim 3 wherein the polymer is a polyoxymethylene.

10. A process according to Claim 9 wherein the hollow workpiece is heated to a temperature from 80°C to 170°C.

11. A process according to Claim 3 wherein the polymer is a vinylidene fluoride polymer.

12. A process according to Claim 11 wherein the hollow workpiece is heated to a temperature from 80°C to 165°C.

13. A process according to Claim 3 wherein the polymer is a polyester.

14. A process according to Claim 13 wherein the hollow workpiece is heated to a temperature from 55°C to 120°C.

15. A process according to any preceding claim wherein the hollow workpiece comprises a filler.

16. A process according to any preceding claim wherein the hollow workpiece is essentially unoriented before deformation.

17. A process according to any preceding claim wherein the hollow workpiece is an open-ended elongate workpiece of substantially constant cross-section.

18. A process according to Claim 17 wherein the hollow workpiece has an axis of symmetry.

19. A process according to Claim 18 wherein the hollow workpiece has a circular, elliptical, square, rectangular or triangular cross-section.

20. A process according to any preceding claim wherein at the die and, optionally, downstream therefrom there is positioned within the hollow workpiece a former having a cross-sectional area of at least the initial internal cross-sectional area of the hollow workpiece.

21. A process according to any preceding claim wherein the die is heated.

22. A process according to any preceding claim wherein the oriented thermoplastic material passes through a heated chamber downstream from the die.

23. A process according to any preceding claim wherein the hollow workpiece is drawn through the die in the solid phase at a nominal deformation ratio of at least 3:1.

24. A process according to Claim 23 wherein the draw speed is greater than 50 cm min^{-1}.

25. A process according to Claim 23 or 24 which is continuous.

26. A toughened oriented polymer material prepared by the process of any preceding claim.

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GB 1327140

(58) Field of search
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(54) **Solid phase deformation process**

(57) Improved mechanical properties may be obtained by the solid phase deformation, through a die, of a workpiece comprising an orientable thermoplastic polymer which is initially present, at least in part, in an extended chain crystalline morphology.

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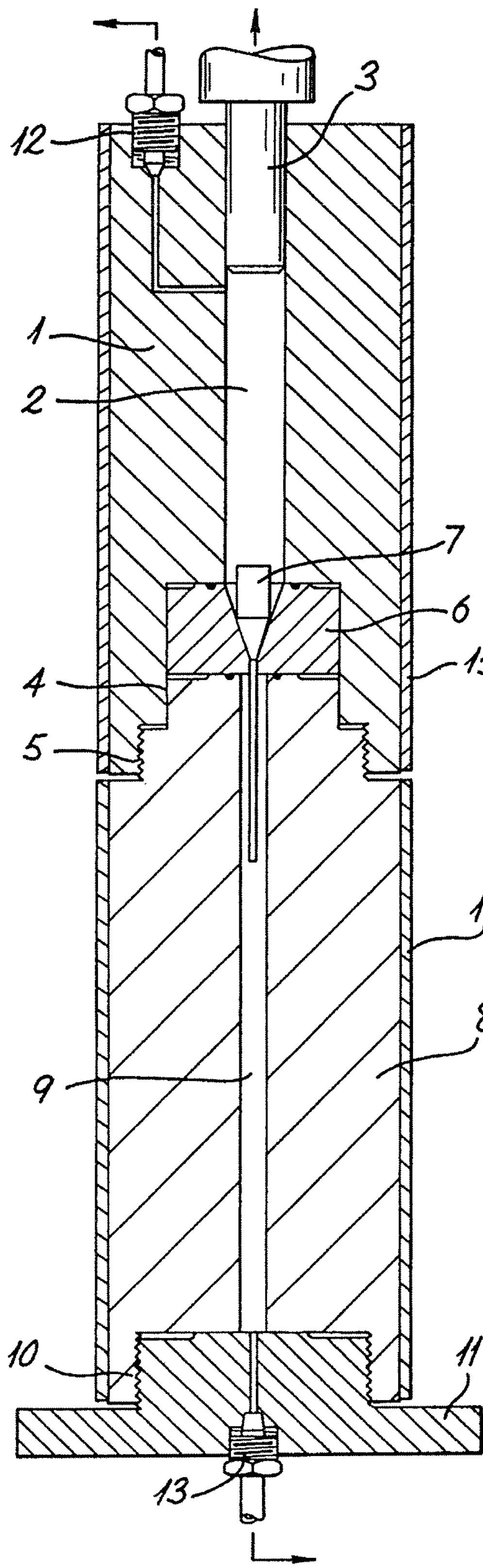
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SPECIFICATION

Solid phase deformation process

This invention relates to solid phase deformation processes; more particularly, this invention relates to the solid phase deformation of orientable, semi-crystalline, thermoplastic polymeric materials; and to improve polymeric materials obtained thereby.

During the last twenty years, a very substantial amount of research has been effected into the improvement of, principally, the mechanical properties of flexible polymers by orientation. The required very high orientation of the molecular chains of flexible polymers, notably linear polyethylene, may be obtained either by preventing the formation of chain folded crystallites, as with precipitation from solution in an extensional flow regime, or by transforming a previously chain folded morphology into one comprising extended molecular chains, as with mechanical deformation: see, for example, our UK Patent Nos. 1480479 and 2060469B.

The latter class of procedures has the substantial advantage that, particularly in the case of filament spinning and drawing, existing industrial practice can integrate the procedures with comparatively small change. A disadvantage, however, notably in relation to polymeric stock of substantial cross-section is the amount of processing space necessarily required by the large deformation ratios which are dictated.

This invention seeks to provide a solid phase deformation process in which higher effective deformation, at given deformation ratios, than was hitherto available is manifest.

According, therefore, to one aspect of this invention there is provided a process for the deformation of a workpiece comprising an orientable, thermoplastic polymer by passage in the solid phase through a die having both an entry side and exit side, which process comprises providing the workpiece comprising the orientable, thermoplastic polymer which is initially present, at least in part, in an extended chain crystalline morphology at the entry side of the die; causing the workpiece to deform in the solid phase through the die; and collecting the deformed workpiece from the exit side of the die.

Preferably, the process effects a reduction in the bulk cross-sectional area of the workpiece. (By 'bulk cross-sectional area' is meant the area of the bulk of the workpiece normal to the machine direction.) Preferably, the die is a reducing die.

Not all polymers are capable of existing with an extended chain crystalline morphology; however, the process of the present invention is applicable to linear polyethylene and fluorinated vinyl polymers; for example polyvinylidene fluoride and polytetrafluoroethylene, the latter existing in an extended chain crystalline morphology at standard temperature and pressure. From a commercial standpoint, the process of the present invention is of particular importance in relation to linear polyethylene, preferably having a weight average molecular weight ($\bar{M}_w$) from 50,000 to 3,000,000, especially from 100,000 to 1,500,000. In contrast to other solid phase deformation processes, the process of the present invention is facilitated by the use of high $\bar{M}_w$ polymers; for example, linear polyethylene having an $\bar{M}_w$ greater than 750,000. Where the process of the present invention is utilised in relation to polyvinylidene fluoride, it is desirable that the polymer has an $\bar{M}_w$ from 200,000 to 800,000, preferably 250,000 to 400,000.

The term "workpiece" as used herein includes bars, strips, rods, tubes and other cross-sections of solid or hollow stock. The term includes both billets and other forms of stock of greater length; indeed, continuous stock, which may be formed as the process is performed, may be utilised.

The orientable, semi-crystalline, thermoplastic workpieces used in the process of this invention may be filled. Examples of useful fibrous fillers include glass, asbestos, metal, carbon and ceramic whiskers, such as those formed from silicon carbide. Examples of useful laminar fillers include mica, talc and graphite flakes. Chalk and fly ash may also be included. The amount of filler which may advantageously be included depends on the nature of the filler, but up to 50% by weight, preferably less than 30%, especially less than 20% may be incorporated.

It is preferred that a major amount of the polymer is present in an extended chain crystalline morphology before the deformation process of this invention is effected.

In accordance with a preferred embodiment of this invention the workpiece is caused to deform through the reducing die in the solid phase by hydrostatically extruding it therethrough. Draw-assisted hydrostatic extrusion, as described in our UK Patent No. 1480479, may be utilised with advantage. The net hydrostatic pressure (that is, the difference between the applied extrusion pressure and the applied extrudate pressure which, as explained subsequently, need not be substantially standard pressure) for extrusion to occur will, at a given extrusion temperature, increase with increasing extrudate pressure and will, at a given extrudate pressure, decrease with increasing temperature. A value from 0.2 to 3.0 kbar, preferably from 0.5 to 2.0 kbar, for example 1 kbar, is found to be suitable.

It is also feasible to deform the workpiece by drawing it through the reducing die without

hydrostatic pressure.

It is also preferred that the reducing die temperature is above the T_g of the polymer but below the melting point of the polymer at the ambient pressure at which the deformation is effected. As the deformation temperature increases (and it may increase to high values where high ambient pressures are used, it being appreciated that the melting point of the polymer increases by approximately 20°C for each kbar of applied pressure) above 200°C process control becomes increasingly difficult. It is, therefore, preferred that the extrusion is effected at an atmospheric ambient pressure and at a temperature from 90°C to 120°C, in the case of linear polyethylene. The polymer may also be dielectrically heated, as disclosed in EPA 0084274.

While nominal deformation ratios (R_N) of up to 50, for example 20, have been obtained with linear polyethylene it is a feature of the process of the present invention that more effective deformation is attained. That is, a given enhancement of a physical property may be attained at a lower deformation ratio by the present process. Accordingly, R_N is suitably from 4 to 12, preferably from 5 to 10; for example 8.

This invention also provides a process as herein described wherein the extended chain crystalline morphology is first imparted to the polymer by subjecting the workpiece to a temperature and pressure at which the polymer crystallises with this morphology. This aspect of the invention may be effected separately, as is preferred, or may be effected in the extrusion apparatus, as subsequently described, immediately prior to deformation, it being understood that the apparatus should be capable of withstanding a pressure of 5 kbar at a temperature of 275°C. Chain extended crystalline morphology is found to be imparted to the polymer at pressure above 3.5 kbar (but it is not usually necessary to exceed 4.8 kbar) and temperature above 220°C (in the case of linear polyethylene) and 207° (in the case of polyvinylidene fluoride).

The presence of chain extended crystalline morphology is manifest by an increased melting point (DSC) and a higher density. In the case of linear polyethylene these are, respectively, >140°C and >0.98 g cm^{-3}.

The invention also provides an oriented, semi-crystalline, thermoplastic polymer prepared by the process of the present invention. This invention further provides oriented linear polyethylene which has been deformed to a deformation ratio not greater than 20; for example 12, and which has an axial modulus of at least 15 GPa; for example, of at least 10 GPa.

Furthermore, this invention provides a set hydraulic cementitious or organic thermoset mass which incorporates an oriented polymer prepared by a process of the invention.

The invention will now be further described, by way of example, with reference to the accompanying drawing, in which:

the sole figure represents an axial cross-section of the annealing and extrusion apparatus used in the process of the present invention.

In the drawing, the apparatus comprises a generally cylindrical hydrostatic extrusion vessel 1 containing an axially aligned chamber 2, having a diameter of 20 mm and an effective length of 170 mm, which is closed at an upstream end by an internally slidable piston 3 in a fluid-tight fit therewith which piston is connected externally to a load cell (not shown) of a universal testing machine. The downstream end of the chamber is formed with two, internal, axially symmetric shoulders 4 and 5 which are each threaded to receive a threaded conical reducing die 6 in which a workpiece 7 is seated and a threaded upstream end of an extrudate vessel 8 by which the reducing die is effectively clamped in position and which comprises an axially aligned extrudate chamber 9, having a diameter of 8 mm and an effective length of 220 mm. The downstream end of the extrudate vessel is formed with an internal shoulder 10 which is threaded to receive a threaded end closure 11. Both the extrusion and the extrudate vessels have a first and second port 12 and 13, respectively, which communicate with pressure varying systems (not shown); and are both provided with circumferential band heaters 14 and 15 enabling the tooling temperature to be maintained within 2°C.

The use of the apparatus is described in the following Example which illustrates the invention.

EXAMPLE

Preparation of the billet and its pressure annealing

High density polyethylene (Rigidex 006/60 *ex* BP Chemicals Ltd. $\bar{M}_w = 135{,}000$; $\bar{M}_w = 25{,}500$; "RIGIDEX" is a registered Trade Mark) was melt extruded into a billet mould and cooled slowly with isostatic compaction. A number of cylindrical billets were so produced having a density ca. 0.97 g cm^{-3}. A nose was then machined on each billet so that it would accurately mate with the reducing die as shown in the accompanying drawing. Three reducing dies having bore diameters of 2.5, 3.1 and 5.0 mm were used; the conical semi-angle was 15° in each case.

Each billet was, in turn, urged into position in the reducing die; the tooling was assembled as shown in the accompanying drawing; and the chambers filled with a silicone oil (DC 550 *ex* Dow Corning), and suitably bled. A hydro-pump was used to raise the oil pressure in both

vessels to a mean value of 3 kbar at the ambient temperature, a slighly higher pressure being maintained in the extrusion vessel which was sufficient to retain the billet in position without its undergoing extrusion. Thereafter, the band heaters were energised, the heat causing expansion of the silicone oil and a further increase of pressure: at a temperature of 200°C the pressure had attained 4.5 kbar. Heating was continued with the pressure being maintained at about 4.5 kbar, either by withdrawing the piston (though it is the primary purpose of the piston, in this phase of the process, to act as a static seal) or releasing some of the silicone oil *via* the ports, until an equilibrium temperature of 240°C was attained. The billet was then annealed at this temperature and pressure for 1 hour, the whole procedure to the termination of annealing taking about 3 to 4 hours. The band heaters were next switched off and the extrusion vessel allowed to cool, while maintaining the pressure at 4.5 kbar, to about 160°C. After this, both the temperature and pressure were permitted gradually to fall; when the temperature had fallen to 100°C, the residual excess pressure was released by venting the ports.

Hydrostatic extrusion of the pressure annealed billet

The band heaters were re-energised, the silicone oil being raised to an equilibrium temperature of 100°C. Load was then applied to the piston to urge it into the extrusion vessel at a constant speed. The workpiece (or billet) was extruded through the die at an extrusion speed of up to 200 mm min^{-1}; for example, 5 mm min^{-1}.

In some of the experimental runs effected with others of the prepared billets a pressure was applied to both the extrusion and extrudate vessels to give a high ambient pressure, the back extrusion pressure in the extrudate vessel being maintained constant during extrusion by venting port 13.

At the termination of the extrusion, the temperature was, in each case, allowed to fall to below 100°C before the excess pressure was released and the product extracted.

The axial modulus of the extruded products was determined by the 3-point bend method at strains >0.1% taking the response 10 seconds after application of the load. The results are shown in the following Table.

NOMINAL EXTRUSION RATIO (R_N)	EXTRUSION TEMPERATURE (°C)	EXTRUDATE BACK PRESSURE (kbar)	AXIAL MODULUS (GPa)	
			(a)[1]	(b)[2]
5	100	0	15.9	7.9
10	100	0	32.6	17.5
10	140	2.0	33.8	18.3
10	160	3.0	33.7	-

[1]Pressure annealed billets
[2]Billets prepared and deformed in accordance with the disclosure of UK Patent No. 1480479

It will be apparent from the above results that pressure annealing effected before extrusion of the workpiece enables a much more effective deformation to be attained; that is, for a given deformation ratio a much greater increase in axial modulus is obtained. It will also be apparent that application of substantial pressure after annealing has no comparable effect.

CLAIMS

1. A process for the deformation of a workpiece comprising an orientable, thermoplastic polymer by passage in the solid phase through a die having both an entry side and an exit side, which process comprises providing the workpiece comprising the orientable, thermoplastic polymer which is initially present, at least in part, in an extended chain crystalline morphology at the entry side of the die; causing the workpiece to deform in the solid phase through the die; and collecting the deformed workpiece from the exit side of the die.

2. A process according to Claim 1 wherein the polymer is linear polyethylene, polyvinylidene fluoride or polytetrafluoroethylene.

3. A process according to Claim 2 wherein the polymer is linear polyethylene.

4. A process according to Claim 3 wherein the linear polyethylene has a weight average molecular weight ($\bar{M}_w$) from 50,000 to 3,000,000.

5. A process according to Claim 4 wherein $\bar{M}_w$ is from 100,000 to 1,500,000.

6. A process according to Claim 2 wherein the polymer is polyvinylidene fluoride.

7. A process according to Claim 6 wherein the polyvinylidene fluoride has an $\bar{M}_w$ from 200,000 to 800,000.

8. A process according to any preceding claim wherein the workpiece is formed as a bar, strip, rod or tube.

9. A process according to any preceding claim wherein polymer is filled.

10. A process according to any preceding claim wherein the workpiece is hydrostaticaly extruded through the reducing die.

11. A process according to Claim 10 wherein the hydrostatic extrusion is draw-assisted hydrostatic extrusion.

12. A process according to any of Claims 1 to 9 wherein the workpiece is drawn through the reducing die without hydrostatic pressure.

13. A process according to Claim 10, 11 or 12 wherein the reducing die temperature is above the T_g of the polymer but below the melting point of the polymer at the ambient pressure at which the deformation is effected.

14. A process according to any preceding claim wherein the ambient pressure at which the extrusion is effected is atmospheric pressure.

15. A process according to any preceding claim wherein the deformation ratio is from 4 to 20.

16. A process according to Claim 15 wherein the deformation ratio is from 5 to 10.

17. A process according to any preceding claim wherein the extended chain morphology is first imparted to the polymer by subjecting the workpiece to a temperature and pressure at which the polymer crystallises with this morphology.

18. A process according to Claim 17 wherein the polymer is linear polyethylene and the workpiece is heated to a temperature above 220°C while being maintained in the solid phase.

19. A process according to Claim 17 wherein the polymer is polyvinylidene difluoride and the workpiece is heated to a temperature above 207°C while being maintained in the solid phase.

20. A process according to any of Claims 17 to 19 wherein the workpiece is subjected to a pressure of at least 3.5 kbar.

21. An oriented, semi-crystalline, thermoplastic polymer prepared by the process of any preceding claim.

22. Oriented linear polyethylene which has been deformed to a deformation ratio not greater than 12 and which has an axial modulus of at least 15 GPa.

23. A set hydraulic cementitious or organic thermoset mass which incorporates an oriented polymer according to Claim 21 or 22.

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B29C 55/26

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(58) Field of search
UK CL (Edition J) **B5A AA1 AD31 AT17S AT18P, B5B**
INT CL⁴ **B29D**

(54) **Tubular materials**

(57) Tubular workpieces of oriented polymers such as polyethylene polyester and PVC are formed by drawing a workpiece over an expanding former in the absence of any external force perpendicular to the axis of the workpiece. The process does not use any liquid lubricant. It enables greater degrees of expansion and hence orientation in the direction perpendicular to the axis to be achieved and results in products of improved appearance e.g. transparency and strength.

Fig. 1

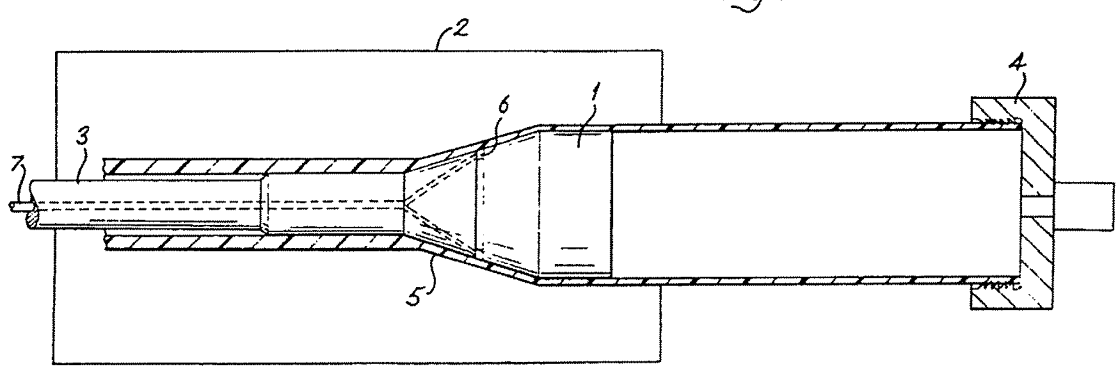

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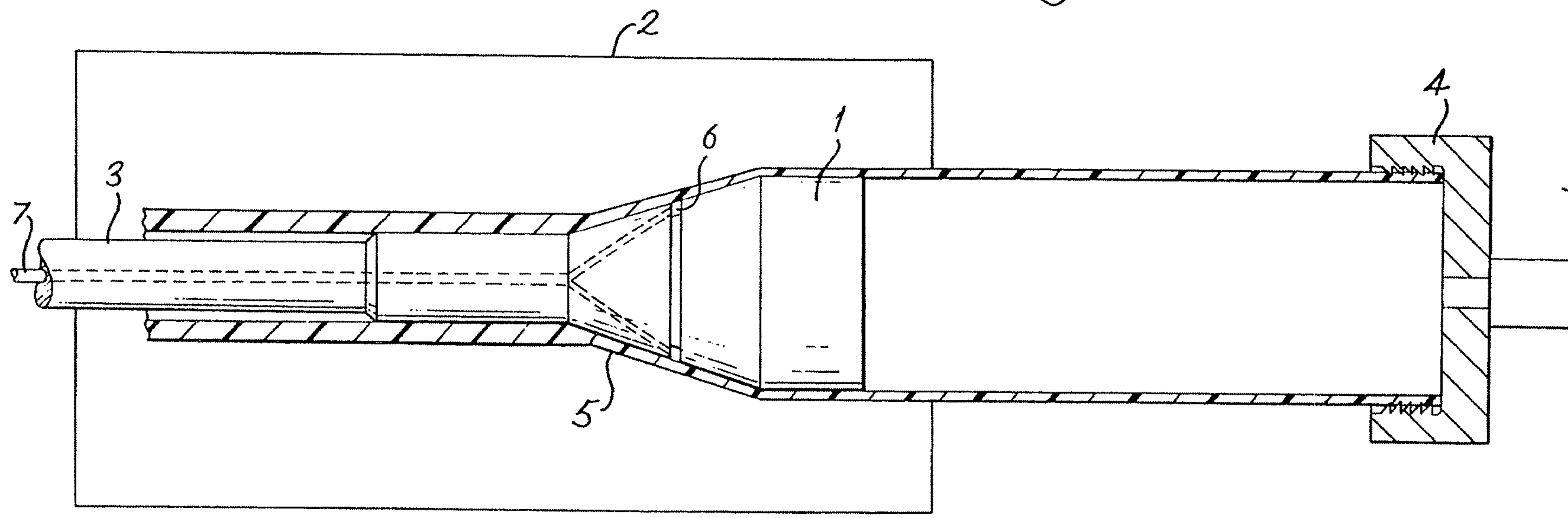
Fig. 1



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TUBULAR MATERIALS

This invention relates to processes for the production of tubular materials of an orientable thermoplastic polymer by solid phase deformation and to the products of those processes.

Previous attempts to introduce biaxial orientation into tubular materials formed from orientable thermoplastic polymeric materials by drawing them over an expanding former have involved only a limited degree of expansion in the hoop direction i.e. in the direction perpendicular to the axis of the tube. British Patent 1456222 describes a process and apparatus used to draw a tube of thermoplastic polymer over an expanding former in order to calibrate the internal dimensions of the tube. The processes described require the application of a liquid lubricant to the inner surface of the workpiece prior to its passage over the former. In our British Patent 2156733 we have described processes in which the tubular material is drawn simultaneously through a die and over an expanding former.

We have now discovered that uniform biaxially oriented products can be produced by processes which comprise drawing the tubular material over an expanding former without the need to apply a liquid lubricant. Such procedures are advantageous in that the products may have a greater degree of orientation in the hoop direction and correspondingly uniformly greater strength in that direction than has previously been attainable. Furthermore insofar as they involve only drawing the tubular material over a former they offer advantages in simplicity of operation and in the improved appearance of the product.

Accordingly from one aspect our invention provides a process for the production of a biaxially oriented tubular material which comprises drawing a hollow workpiece comprising an orientable thermoplastic polymer over an internally positioned expanding former without the application of a liquid lubricant to the interior of the workpiece which is characterised in that the deformation of the workpiece is carried out in the absence of any external force acting in a direction which is perpendicular to the axis of the workpiece.

The term "hollow workpiece" as used herein includes tubes and other cross-sections of hollow stock. The term includes both billets and other forms of stock of greater length. Continuous stock, which may be formed as the process is performed, may be utilised. Examples include open-ended elongate workpieces of substantially constant cross-section, desirably with an axis of symmetry; for example, hollow workpieces of circular, elliptical, square, rectangular or triangular cross-section.

The orientable thermoplastic polymers may be a semicrystalline polymer such as polyethylene, polypropylene or polyvinylidene fluoride, an amorphous crystallising polymer such as polymethylmethacrylate or a crystallisable polymer such as polyvinylchloride, polyesters or polycarbonates. Examples of preferred classes of such polymers are unsubstituted or mono- or poly- halo-, for example chloro- or fluoro- substituted vinyl polymers, unsubstituted or hydroxy-substituted polyesters, polyamides, polyetherketones and polyacetals. Specifically, linear homo- or copolymers of ethylene or propylene with at least one comonomer; a vinyl chloride polymer; a vinyl fluoride polymer or a vinylidene fluoride polymer; PHB; PEEK; or a homo- or co-polyoxymethylene may be utilised.

The hollow workpiece is preferably essentially unoriented before deformation. The term "essentially unoriented" as used herein means that the hollow workpiece has incurred no orientation other than that minor amount which might be induced during formation of the workpiece, (including orientation produced in the semi-molten state) for example during billet moulding or melt extrusion, or during any subsequent shaping thereof, for example by machining, prior to its passage over the former. However, workpieces which have been oriented to a considerable degree may be advantageously utilised in the processes of the present invention. For example workpieces which have been produced by extrusion through a die or by deformation in the solid phase through a die may be utilised.

Where it is not possible to use the polymer as received as a hollow workpiece, the workpiece may be formed either in the batch or continuously. In either case care should be taken to ensure that the workpiece cools at an appropriate rate so that the resulting hollow workpiece will be without defects. The techniques for forming such workpieces are well known in the art. For example in the case of a hollow workpiece formed from polyethylene in a batch process as a billet, the following general methods have been found to be suitable. The polymer may be melted in a screw extruder; extruded or injected into a billet mould at a temperature about 30°C above its melting point and cooled under elevated pressure for 5 hours, or it may be melted in an extruder; extruded or injected into a cold billet mould; transferred to an oven for 4 hours under ambient pressure at a temperature below its melting point but above its crystallisation temperature; and thereafter allowed to cool in the oven after the heating has been switched off. The polymer may also be injection moulded into an air or water cooled billet mould. Progressive immersion in the cooling fluid is preferred, thereby ensuringthat solidification of the polymer takes place from the bottom of the mould thereby preventing the formation of internal voids due to shrinkage. A hollow workpiece may be formed in the batch by including a mandrel of appropriate cross-section, usually coaxially, in the mould. Alternatively, stock of circular or other hollow cross-section may be produced continuously using one of several processes known to those skilled in the art.

For any particular polymer a steady state process may be obtained by adjusting the parameters of the process. The actual values will depend on the nature of the polymer and the dimensions of the polymer before and after deformation. In particular we have discovered that the minimum hoop draw ratio for any particular polymer should be sufficiently high so as to ensure that a uniform product is produced. Preferably the axial draw ratio is also maintained at a level which ensures this.

Where a non-uniform product is produced under particular conditions these ratios can and preferably are increased. The actual values required to produce a uniform product of a particular polymer may readily be determined by routine experiment.

The hoop draw ratio is defined as the ratio of the final hoop dimension to the initial hoop dimension and the axial draw ratio is the ratio of the initial bulk cross sectional area of the hollow workpiece to the final bulk cross sectional area of the product. The hoop draw ratio is conventionally expressed as the ratio of the maximum dimension of the product to maximum dimension of the workpiece. Because the walls of a tubular workpiece have a finite thickness the hoop draw ratio can be expressed either as the inner hoop draw ratio (i.e. the ratio of the inside diameter of the product to the inside diameter of the workpiece) or the outer hoop draw ratio (i.e. the ratio of the outside diameter of the product to the outside diameter of the workpiece. The inner hoop draw ratio will always be the larger.

For polyolefins and in particular linear homo and co polymeric polyethylenes the preferred inner hoop draw ratio is at least 1.2 and more preferably at least 1.5 and most preferably at least 2.0. The preferred axial draw ratio is at least 2 and preferably greater than 3. The outer hoop draw ratio may be less than 1 but is preferably at least 1 and more preferably at least 1.5 or 2.0. The ratio of the axial draw ratio to the inner hoop draw ratio is preferably at least 1 and less than 4, most preferably less than 2. For polypropylene it may be preferable to utilise large axial draw ratios even up to 7 or 8 and the ratio of the axial draw ratio to the hoop draw ratio is correspondingly increased.

For these polymers the hollow workpiece is desirably heated to a processing temperature within 60°C of the melting point of the polymer prior to deformation. More particularly for polyethylene polymers having a weight average molecular weight of

from 50,000 to 150,000 the temperature is preferably from 70°C to 100°C and for polymers having a weight average molecular weight of above 300,000 from 70 to 120°C. For linear homo- and copolymers of polypropylene of weight average molecular weight from 150,000 to 800,000 the hollow workpiece is desirably heated to a temperature from 20°C to 170°C, preferably 90°C to 130°C. The processing temperature is only a nominal temperature since the process is not isothermal but should be within the range which the polymer is amenable to deformation.

The processes of the invention find particular application in the production of tubular polyolefin materials wherein the thickness of the walls of the product tube is from to 0.1 to 5.0 mm.

By "bulk cross sectional area" is meant the area of the polymeric material substantially normal to the machine direction. Thus for tubular workpiece having an exterior diameter D_2 and an interior diameter D1 the bulk cross sectional area is

$$\pi \left(\frac{D_2^{2'} - D_1^2}{4} \right)$$

A preferred class of polyesters is those which are derivable from the reaction of at least one polyhydric alcohol, suitably a linear polyhydric alcohol, preferably a diol such as a linear C_2 to C_6 diol, with at least one polybasic acid, suitably a polycarboxylic acid. The alcohol is preferably an alicyclic or aliphatic such alcohol; for example, cyclohexane-dimethanol or a linear C_2 to C_6 alkylene diol such as ethylene glycol, 1,3-propylene glycol or 1,4-butylene glycol, especially ethylene glycol. The acid is preferably an aromatic, alicyclic or aliphatic such acid; for example a mono- or poly carbocyclic aromatic acid such as an aromatic dicarboxylic acid e.g. o, m-, or terephthalic acid; 2,6- or 1,5-naphthalene dicarboxylic acid or 1,2 dihydroxybenzoic acid especially terephthalic acid.

Examples of suitable polyesters include polyethylene 2,6-naphthalate, polyethylene 1,5-naphthalate, polytetramethylene 1,2-dihydroxybenzoate, polyethylene terephthalate, polybutylene terephthalate and copolyesters, especially of ethylene terephthalate.

With polyesters the inner hoop draw ratio achieved is preferably at least two and preferably at least 3. At the same time the preferred axial draw ratio is at least two and preferably at least three. The processing temperature is preferably from 55 to 110°C or even 55 to 120°C.

The processes of the present invention find particular application in the production of tubular materials comprising polyesters wherein the thickness of the wall of the product tube is from 0.2 to 0.6 mm. Such tubes are preferably produced from tubular billets utilising a deformation ratio of from 2 to 4.

For homo- or copolyoxymethylene a draw temperature of 80°C to 170°C, preferably 150°C to 170°C is suitable and for vinylidene fluoride polymers a draw temperature of from 80°C to 165°C is suitable .

For vinyl chloride polymers especially polyvinyl chloride itself the preferred axial and hoop draw ratios are at least 1.2 preferably at least 1.5 or 2.0. Values of not greater than three may also be preferred. The ratio of the axial draw ratio to the inner hoop draw ratio may be less than unity and is preferably in the range 0.5 to 1.0.

The processing temperature may be further controlled by utilising a heated former and/or a temperature controlled chamber which extends downstream. Certain polymers may also be heated by subjecting them to a dielectric field, as disclosed in EPC 0084274 and US 3364294.

It is feasible to use draw speeds greater than 200 cm min^{-1} in the drawing process of this invention. Speeds of 50 cm min^{-1} or more are preferred. Lower draw speeds may be used if desired.

The process may be operated by drawing the workpiece directly over the surface of the former. However, it may be preferred to lubricate the surface of the former with a non-liquid lubricant as this can improve the quality of the interior surface of the workpiece and also serve to reduce the force required to draw the workpiece. Conveniently the surface is lubricated by use of air (which is preferably heated to an appropriate temperature). These advantages may also be achieved by varying the nature of the former, e.g. by utilising a former whose surface is formed by a multiplicity of small rollers or spherical elements.

The improved surface properties are of particular relevance to processes which utilise workpieces formed from transparent polymers. The processes of the present invention find particular application to the production of transparent products since the exterior surface of the workpiece need not come into contact with the interior surface of a die as is the case in the process of our UK Patent 2156733. Processes for the production of transparent workpieces in which the exterior surface of the hollow workpiece does not contact another solid surface form a preferred aspect of the present invention. The use of a lubricated surface on the former represents a preferred aspect of this embodiment.

In some circumstances it may be preferable to employ a die having an internal diameter equal to the external diameter of the workpiece to act as a guide member to support the workpiece prior to its being drawn over the former. Contact with the surface of such a guide may detract from the surface properties of a transparent workpiece and is thereby less preferred. However, when utilising opaque workpieces or transparent workpieces intended for use in non-decorative applications, the use of such a guide may well be convenient.

In performance of the invention a nose formed on the hollow workpiece is advanced to protrude beyond the former and is secured to tensioning means applied from the exit side thereof.

A suitable arrangement includes a hauloff comprising a pair of serrated jaws in which the nose is gripped; a high tensile cable one end of which cable is attached to the jaws, the other to a winch or a loading station to which a turning moment or mass may be applied thereby applying a draw tension to the nose. The hauloff may also comprise, instead of a cable, any tension transmitting means used in the metal drawing art including a chain, a rack and pinion mechanism, a screw mechanism and a hydraulically operated draw mechanism. The hauloff may further comprise a pair of continuous contra-rotating friction belts, generally known as a "caterpillar" ("CATERPILLAR" is a registered Trademark).

The draw tension should be sufficient to draw the hollow workpiece over the former but insufficient to cause tensile failure of the article; that is, the draw tension should be such that the true stress at any point of the product does not exceed its fracture stress at that point. A suitable maximum value of draw tension may readily be determined by routine experiment.

After a grippable length of the hollow workpiece has been drawn over the former any unsuitably oriented part of its nose may be removed and the oriented grippable length re-gripped thereby enabling a higher initial load to be applied.

A batch process may be converted to a semi-continuous one by putting the upstream end of the deforming hollow workpiece and the downstream end of stock of the same cross-sectional both in contact with a hot, stainless steel plate; removing the plate and welding the two polymer surfaces. Preferably such a weld should be at an angle of 45°C or less to the axis of the stock.

The invention will now be described by way of example by reference to the accompanying drawings in which:-

Figure 1 represents a schematic side elevation of the apparatus diametrically sectional along the machine direction.

In the drawing the apparatus consists of a former 1 and upstream thereof an oven 2. The former 1 is supported by rod 3. Hauloff jaws 4 are positioned downstream from the former 1 and are connected to the winch (not shown). The former has an annular slit 6 connected to pipe 7.

In use the initial hollow workpiece 5 which has been machined at one end to provide a nose is inserted over the former 1 and rod 3. The nose is gripped in the jaws 4 and load applied slowly at first so that the plastic strain is increased without causing tensile failure. After this start-up a steady drawing speed at a steady drawing load is established.

The invention is illustrated by the following Examples:-

Example 1

The workpiece comprised a tube of isotropic polypropylene (ICI grade GSE 108) having an internal diameter of 18.5 mm and an external diameter of 26.5 mm.

As a preliminary operation a belled end was formed on one end of the tube by heating that end to a temperature of 140°C and inserting a hot metal plug in the shape of a taper nosed cylinder into the bore of the tube. The end of the tube and the plug were immersed in hot oil until the end had deformed sufficiently.

The tube was then mounted in the apparatus illustrated in Figure 1. The tube was drawn over a former having a maximum diameter of 70 mm and a cartridge heater through which additional heat could be applied. The tube was drawn at a speed of 13 cm min^{-1} at a draw temperature of 135°C and using a draw force of 1.55 kN.

The drawn tube was substantially uniform throughout its length having an exterior diameter of 62 mm and a wall thickness of 0.225 mm. The hoop draw ratio of the outer surface was 2.25. The axial draw ratio was 6.5.

The 10 sec creep modulus at 0.1% strain of samples cut from the drawn tube was determined for the axial and hoop direction

using the standard dead loading creep method described by Gupta and Ward (V.B. Gupta and I.M. Ward - J. Macromol. Sci. B1 373 1967). The 10 sec creep modulus in the axial direction was 3.7 GPa and in the hoop direction 1.7 GPa.

Example 2

A tubular billet having an external diameter of 25mm and an internal diameter of 17mm of a clear amorphous copolyester (Eastmann 9921) was first deformed so as to provide a belled nose. The tube was placed in an oven at a temperature of 110°C in such a way that a zone of a length of approximately 15 centimetres was heated. After 5 minutes the tube was removed and quickly inflated with room temperature compressed air to a pressure of 620 KN/m^2 whereupon a bubble is blown in the heated part. After depressurising and cooling one end of the bubble is removed so as to produce a belled end on the tube.

The tube was then mounted in the apparatus illustrated in Figure 1 Air heated to a temperature of 95°C was passed through the slit 6 via the pipe 7 so as to float the tube above the surface of the former. The air pressure used was 275 KN/m^2 and the air flow was 40 cubic feet per hour.

The oven was maintained at a temperature of 90°C throughout the drawing process. The tube was drawn at a speed of 20 cm/min using a draw force of 1.5 KN.

The drawn tube was transparent and had an exterior diameter of 76 mm. The wall thickness was 0.31 mm. The axial draw ratio was 3.5. The hoop draw ratio of the outer surface was 3.0.

The Youngs modulus of samples of the drawn tube having a width of 9.8 mm and a gauge length of 10.6 cms were determined in an Instron tensile testing machine at a strain rate of 3.3 x 10^{-4} sec,$^{-1}$.

The stress strain curve was linear up to at least 0.5% strain. The initial modulus for the axial and hoop directions are shown in Table 1.

Table 1

Direction	Initial Modulus (GPa)	Extension to Break (%)
Axial	3.1	63
Hoop	3.0	68

Example 3

A series of billets were formed and drawn using the apparatus as shown in Figure 1. The conditions employed and the results achieved are summarised in Table 2. For ease of comparison the details of Examples 1 and 2 are included in this table.

Table 2

Examples of Die free drawing

Material	Billet size		Mandrel size (mm)	Draw Temp. (^{o}C)	Draw Speed (cm/min)	Draw Force (KN)	Axial draw ratio	Inner surface Hoop draw ratio	Outer surface Hoop draw ratio	
	ID (mm)	OD (mm)								
Polypropylene GSE 108	18.5	26.5	70.0	135	13.0	1.55	6.5	3.33	2.25	Ex 1
	"	"	"	155	6.5	1.10	6.15	3.61	2.5	
	"	"	"	"	65.0	1.10	8.60	2.65	1.85	
PET (Eastman 9221)	17.0	25.0	80.0	90	20.0	1.5	3.5	4.4	3.0	Ex 2
HDPE 00-240	21.0	62.0	62.0	115	3.0	8.0	3.8	2.7	1.03	
	"	"	"	"	50.0	8.0	5.9	2.6	0.97	
PVC (BS 3505 CL7)	32.0	42.0	70.0	100	2.0	2.65	1.47	1.90	1.55	
	"	"	"	"	12.0	2.65	1.55	1.80	1.47	

What we claim is

1. A process for the production of a biaxially oriented tubular material which comprises drawing a hollow workpiece comprising an orientable thermoplastic polymer over an internally positioned expanding former without the application of any liquid lubricant to the interior of the workpiece which is characterised in that the deformation is carried out in the absence of any external force acting in a direction which is perpendicular to the axis of the workpiece.

2. A process according to Claim 1 characterised in that the thermoplastic polymer is a semi-crystalline polymer.

3. A process according to Claim 2 characterised in that the thermoplastic polymer is a polyolefin.

4. A process according to Claim 3 characterised in that the thermoplastic polymer is a polyethylene.

5. A process according to Claim 3 characterised in that the thermoplastic polymer is a polypropylene.

6. A process according to any of Claims 2 to 5 characterised in that the inner hoop draw ratio is at least 1.2.

7. A process according to any of Claims 2 to 6 characterised in that the inner hoop ratio is at least 1.5.

8. A process according to any of Claims 2 to 7 characterised in that the axial draw ratio is at least 2.

9. A process according to Claim 8 characterised in that the axial draw ratio is at least 3.

10. A process according to either of Claims 5 to 9 characterised in that the axial draw ratio is less than 8.

11. A process according to Claim 1 characterised in that the thermoplastic polymer is a crystallisable polymer.

12. A process according to Claim 11 characterised in that the thermoplastic polymer is a polyester.

13. A process according to either of Claims 11 or 12 characterised in that the inner hoop draw ratio is at least 2.

14. A process according to Claim 13 characterised in that the inner hoop draw ratio is at least 3.

15. A process according to any of Claims 11 to 14 characterised in that the axial draw ratio is at least 2.

16. A process according to Claim 11 characterised in that the thermoplastic polymer is poly(vinyl chloride).

17. A process according to Claim 16 characterised in that the inner hoop draw ratio is at least 1.2.

18. A process according to either of Claims 16 or 17 characterised in that the inner hoop draw ratio is at least 1.5.

19. A process according to any of Claims 16 to 18 characterised in that the ratio of the axial draw ratio to the inner hoop draw ratio is in the range 0.5 to 1.0.

20. A process according to any of the preceding claims substantially as hereinbefore described with reference to the foregoing examples.

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(58) Field of search
C3L
Selected US specifications from IPC sub-classes
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(54) Solid phase deformation process

(57) There is disclosed a process for producing a product comprising linear polyethylene which process comprises forming a workpiece which is to be extruded in the solid phase by consolidating under heat and pressure a mass of solid particulate linear polyethylene, subjecting the resulting workpiece to heat treatment under pressure to cause the polyethylene to crystallise in an extended chain morphology with the melting point of the polyethylene being increased to at least 139.5°C and the density to at least 0.98g/cm³, and thereafter deforming the workpiece of the resulting polyethylene in the solid phase, for example by passage through a die, to provide the polyethylene product whereby the workpiece is subjected to a deformation ratio of at least 3, and preferably 3 to 25. The resulting polyethylene may have a Youngs modulus of at least 30 GPa and a melting point of at least 139.5°C.

FIG. 2.

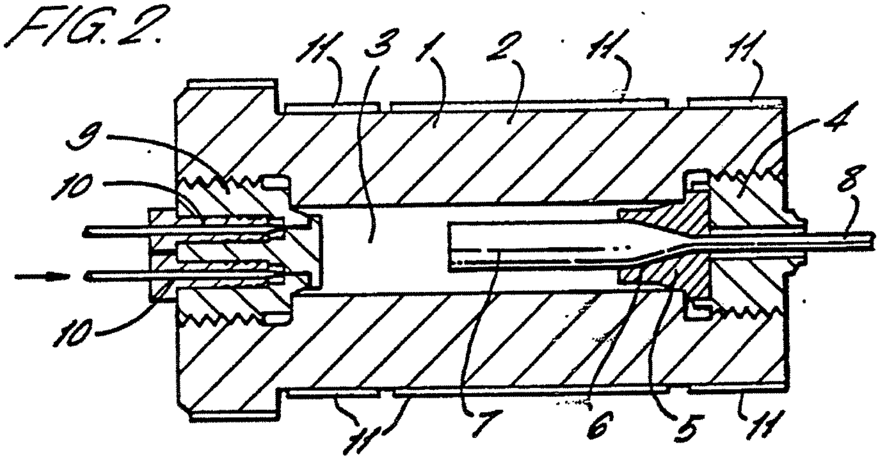

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FIG. 1.

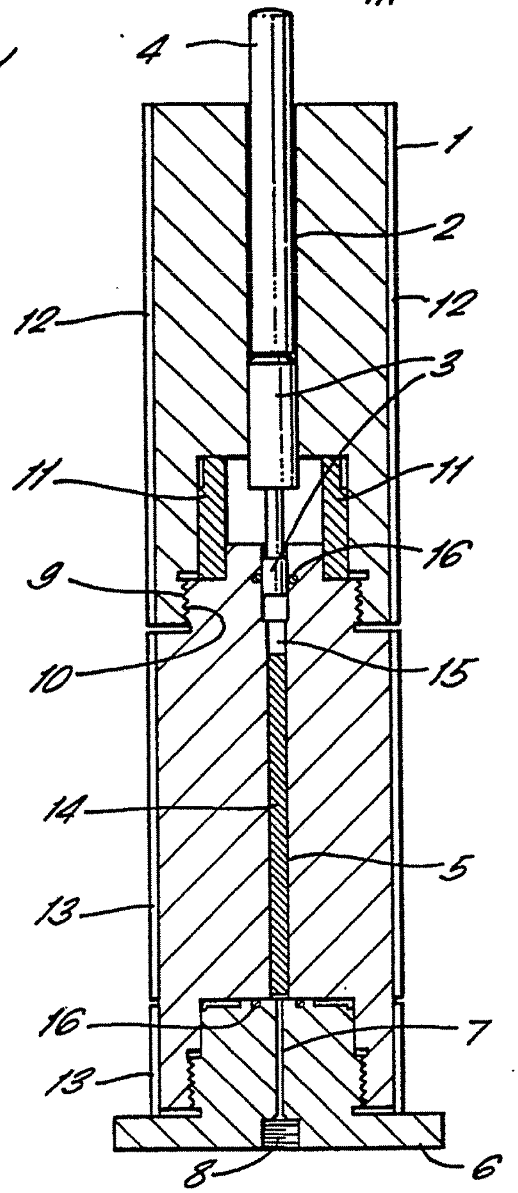
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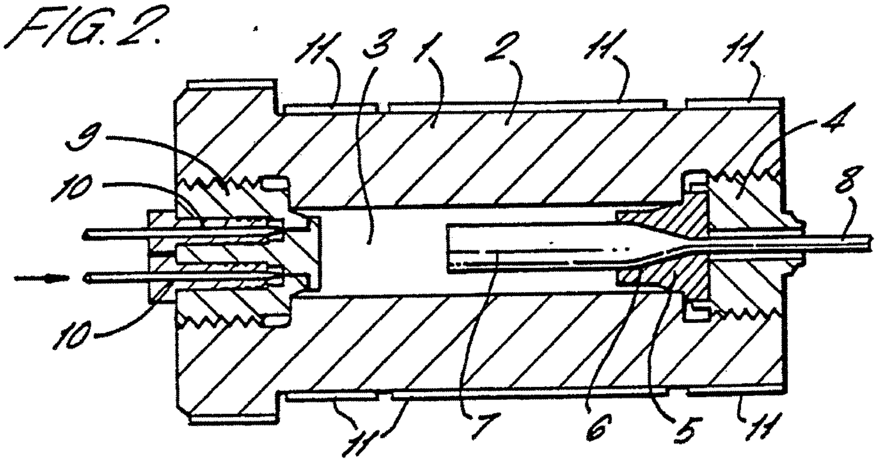
FIG. 2.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SOLID PHASE DEFORMATION PROCESS

This invention relates to solid phase deformation processes, and more particularly to the sold phase deformation of orientable, semi-crystalline, thermoplastic polymeric materials. During the past twenty years or so, a substantial amount of research has been carried out into the improvement of mechanical properties of flexible polymers, principally by orientation. The required very high orientation of the molecular chains of flexible polymers, notably linear polyethylene, may be obtained either by preventing the formation of chain-folded crystallites, as with precipitation from solution in an extensional flow regime, or by transforming a previous chain-folded morphology into one comprising extended molecular chains, as occurs using mechanical deformation; see, for example, UK Patent Specifications Nos. 1480479 and 2060469B.

The above-mentioned prior processes produce a high degree of anisotropy in the structure of the polymer, with concomitant improvement in mechanical properties in the machine direction.

British Patent Specification 2157298A describes and claims a process for the deformation of a workpiece comprising an orientable, thermoplastic polymer by passage in the solid phase through a die having both an entry side and an exit side, which process comprises providing the workpiece comprising the orientable, thermoplastic polymer which is initially present, at least in part, in an extended chain crystalline morphology at the entry side of the die; causing the workpiece to deform in the solid

phase through the die; and collecting the deformed workpiece from the exit side of the die. This specification indicates that the weight average molecular weight (M_w) of polyethylene used in the process may be from 50,000 to 3,000,000. However, it is difficult to process higher molecular weight polyethylene according to the teaching of this prior specification, especially polyethylene with a M_w of greater than 300,000, more particularly greater than 350,000.

The present invention seeks to provide a process comprising a solid phase deformation in which an improvement in mechanical properties of the polyethylene with more satisfactory processing conditions, and constitutes especially an improvement over the process described in Specification No. 2157298A.

According to the present invention there is provided a process for producing a product comprising linear polyethylene which process comprises forming a workpiece which is to be extruded in the solid phase by consolidating under heat and pressure a mass of solid particulate linear polyethylene, subjecting the resulting workpiece to heat treatment under pressure to cause the polyethylene to crystallise in an extended chain morphology with the melting point of the polyethylene being increased to at least 139.5°C and the density to at least 0.98g/cm^3, and thereafter deforming a workpiece of the resulting polyethylene in the solid phase, for example by passage through a die, to provide the polyethylene product whereby the workpiece is subjected to a deformation extrusion ratio of at least 3, and preferably 3 to 25.

The consolidation under heat and pressure of the mass of solid particulate linear polyethylene is carried out under conditions below the melting point of the polyethylene at the applied pressure with the melting only of a surface layer of the particles to form a solid cohered material. The procedure results in the formation of a solid piece of polyethylene which visually has the appearance of a similar extruded product, but it is an advantage of this procedure that the minimum entanglement occurs between molecules of polyethylene of adjacent particles and this has been found to be important in achieving the benefits provided by this invention.

Preferably the workpiece is formed by consolidating a mass of solid particulate linear polyethylene by compression of as-polymerised polyethylene at ambient temperature using high pressure of the order of 150 to 250, preferably about 200 MPa, and thereafter lowering the pressure to 100 to 160, preferably about 130 MPa; thereafter the compacted powder is heated to a temperature of from 130 to 150°C, and preferably about 140°C, whereby the polyethylene powder is consolidated into a compacted workpiece by melting only a surface layer of the particles to a solid cohered material. The polyethylene of the resulting workpiece is then suitable for annealing to produce the chain extended morphology required by the process of this invention.

Preferably, the deformation effects a reduction in the bulk cross-sectional area of the workpiece. (By 'bulk cross-sectional area' is meant the area of the bulk of the workpiece normal to the

machine direction.) This deformation is readily achieved by means of a reducing die. However, deformation in accordance with the invention can be achieved by drawing a workpiece through a pair of opposed pressure rolls.

From a commercial standpoint, the process of the present invention is of particular importance in relation to linear polyethylene having a weight average molecular weight (M_w) from 300,000 or 350,000 to 3,000,000, preferably from 350,000 to 1,500,000, and especially from 750,000 to 1,000,000.

The term "workpiece" as used herein includes bars, strips, rods, tubes and other cross-sections of solid or hollow stock. The term includes both billets and other forms of stock of greater length; indeed, continuous stock, which may be formed as the process is performed, may be utilised.

The workpieces used in the process of this invention may comprise a filler. Examples of useful fibrous fillers include glass, asbestos, metal, carbon and ceramic whiskers, such as those formed from silicon carbide. Examples of useful laminar fillers include mica, talc and graphite flakes. Chalk and fly ash may also be included. The amount of filler which may advantageously be included depends on the nature of the filler, but up to 50% by weight, preferably from 5 to 30%, especially from 5 to 20% may be incorporated into the polyethylene prior to the consolidation of particles to form a workpiece.

In accordance with a preferred aspect of

this invention the workpiece is caused to deform through the reducing die in the solid phase by hydrostatically extruding it therethrough. Draw-assisted hydrostatic extrusion, as described in British Patent Specification No. 1480479, may be utilised with advantage. The net hydrostatic pressure (that is, the difference between the applied extrusion pressure and the applied extrudate pressure) for extrusion to occur will, at a given extrusion temperature, increase with increasing extrudate pressure and will, at a given extrudate pressure, decrease with increasing temperature. A value from 20 to 300 MPa, preferably from 50 to 200 MPa, for example 100 MPa, is suitable.

The workpiece may also be deformed by drawing it through a heated reducing die without hydrostatic pressure. As the deformation temperature increases (and it may increase to high values where high ambient pressures are used as the melting point of the linear polyethylene increases by approximately 20°C for each 100 MPa of applied pressure) above 200°C process control becomes increasingly difficult. It is, therefore, preferred to employ hydrostatic extrusion into an atmospheric pressure with the polyethylene at a temperature from 90°C to 120°C as it undergoes extrusion.

While nominal deformation ratios (R_N) of up to 50, for example 20, have been obtained with linear polyethylene it is a feature of the process of the present invention that more effective deformation is attained. That is, a given enhancement of a physical property may be attained at a lower deformation ratio by the present process starting from particulate polyethylene. Accordingly, R_N is

suitably from 4 to 20, preferably from 8 to 14.

The compacting of the particulate polyethylene may be effected in a separate operation, as is preferred, or may be effected in an extrusion apparatus prior to annealing and deformation, it being understood that the apparatus should preferably be capable of withstanding a pressure of 600 MPa at a temperature of 260°C. Chain-extended crystalline morphology is found to be imparted to the polymer at pressure above 350 MPa (but it is not usually necessary to exceed 480 MPa) and temperatures above 220°C. It is generally preferred to produce the chain-extended crystalline morphology at 450 MPa and 235°C.

The presence of chain-extended crystalline morphology in linear polyethylene is manifest by an increased melting point (DSC) and a higher density: these are, respectively, at least 139.5°C or 140°C and at least 0.98 g/cm^3.

The invention also provides linear polyethylene prepared by the process of the present invention. This invention further provides oriented linear polyethylene having a weight average molecular weight of at least 350,000, and preferably from 350,000 to 1,000,000 which has been deformed to a deformation ratio of from 3 to 20, and which has a Young's modulus of at least 30 GPa and has a melting point of at least 139.5°C; for example 10, and which has a Young's modulus of at least 30 GPa, for example, of at least 35 GPa.

Furthermore, this invention provides a set hydraulic cementitious or organic thermoset mass

which incorporates a reinforcement constituted by linear polyethylene prepared by the process of the invention. The reinforcement may be in the form of rods, monofilaments, tubes, tapes or the like, and may be non-circular in cross-section.

The invention will now be further illustrated by way of examples with reference to the accompanying drawings, in which:

Figure 1 shows in cross-section high pressure annealing apparatus; and

Figure 2 shows in cross-section a hydrostatic extruder.

Referring to Figure 1 there is illustrated high pressure annealing apparatus 1 which comprises an upper cylindrical vessel 2 which is provided with a piston 3 which is provided with a pressure-type seal (not shown) with the surrounding housing. The piston is urged in the downward direction by a ram 4 and a screw-driven universal testing machine (not shown). The entire apparatus as shown in Figure 1 is mounted in the compression zone of the machine. The lower cylindrical vessel 5 constitutes a pressure vessel, the vessel being provided with an end closure 6 which is provided with a central channel 7 to a port 8. The upper vessel 2 and the lower vessel 5 are assembled together in operative position by means of the threaded sections 9 and 10 on the upper and lower vessels 2 and 5, respectively. A cylinder 11 is positioned between the upper and lower vessels 2 and 3. The upper vessel and the pressure vessel are shrouded in separately controlled electrical band heaters 12, 13, which enables a uniform temperature

distribution to be maintained within the pressure vessel. In use a billet of consolidated polyethylene 14 is positioned in the pressure vessel and a silicone fluid 15, such as DC 550 silicone oil, which is introduced into the pressure vessel before fitting the piston 3. Pressurisation of the silicone fluid is achieved by the compressive loading of the piston 3, the lower portion of which is located in the lower vessel during use. The pressure within the pressure vessel is monitored continuously by a foil-gauge pressure transducer (not shown). The transducer is incorporated in a pressure monitoring pipe which is connected into port 8 using standard high pressure fittings. Thermocouple leads monitoring temperature in the region of the billet pass through the pressurised cylindrical hole in the plug and through the pressure monitoring pipe to an insulated plug (not shown). Because the high temperatures and pressures used in the pressure vessel are severe, the seals 16 around the end closure 6 and the piston 3 employ an O ring/mitre ring combination which need frequent replacement. The apparatus shown in Figure 1 was seated on a support stand to enable access for both the thermocouple assembly and the pressure transducer.

PRODUCTION OF WORKPIECE WITH EXTENDED CHAIN MORPHOLOGY

A billet of linear polyethylene was produced by a compaction procedure employing as-polymerised linear polyethylene powder (R-516 ex BP Chemicals Ltd. $\bar{M}_w$ 742,000 and $\bar{M}_n$ 13,600). The compaction equipment comprised a die and dual ram arrangement, the die itself being shrouded by a controlled band heater which enabled a uniform temperature to be achieved within the cavity of the

die. The as-polymerised polyethylene powder was initially compressed by positioning the die with the powder therein within the compression zone of a 300 tonne hydraulic press. The powder was initially compressed to 200 MPa at the ambient temperature of 20°C. The applied pressure was then lowered and maintained at 130 MPa. The band heater around the die was then energized and the heating carried out until after about 40 minutes the polyethylene reached a final equilibrium temperature of 140°C. The pressure and temperature were maintained for a further 10 minute period after which the heater was switched off. The die and the contents were cooled by air jets with the 130 MPa pressure being maintained during cooling to ambient temperature. The product formed as a result of this high pressure compaction procedure was a powder-compacted disc of cohered particles of about 140mm diameter and 20mm in thickness. The disc was machined to provide a billet for high temperature/pressure annealing.

The billet 14 was introduced into the pressure vessel 5 displacing silicone oil which previously filled the vessel 5. The heater was energized and the pressure transducer was allowed to attain a temperature of about 150°C. After 20 minutes the pressure within the vessel was raised to approximately 300 MPa at room temperature. The heaters 12, 13 around both the upper and lower vessels 2, 3 were energized and as the heating proceeded the pressure was allowed to build up until after about 15 minutes a pressure of about 450 MPa was reached.

When a temperature of 230°C was reached the pressure was held constant by approximately

withdrawing the piston. Approximately 40 minutes were required to attain this temperature which was within 5°C of the required annealing temperature; at this point the temperature was raised at about 0.5°C/minute until the annealing temperature of 240°C was reached, and thereafter these conditions were maintained until the billet was annealed. An annealing time of 0.5 hour at 240°C was generally employed.

After the annealing was completed, the heaters of the upper and pressure vessels were switched off and an air fan was employed to cool both vessels while the pressure was held constant. An initial cooling rate of about 5°C/minute was employed. After about 20 minutes the vessels had cooled to about 160°C and the pressure was maintained constant during this period. Thereafter the pressure was not controlled but was allowed to drop with decreasing temperature. Even though the pressure was not held constant at this stage, the drop of pressure was such that an undercooling of 80°C was observed, but no structural changes occurred. The vessels were allowed to cool further to below 80°C before the residual pressure was released and the annealed billet removed from the apparatus. The whole period for this annealing process to provide in the polyethylene the extended chain morphology took between 3 and 4 hours.

HYDROSTATIC EXTRUSION OF THE ANNEALED BILLET

Referring to Figure 2, there is shown in cross-section the hydrostatic extruder 1. It employs a Fielding Platt hydrostatic system capable of

generating up to 7 MPa pressure. The extruder comprises a central barrel 2 which is generally cylindrical and contains a cylindrical pressure chamber 3. One end of the barrel is closed with a plug 4 which is screwed into the end of the barrel. Seated against the plug 4 is the extrusion nozzle 5 which includes a conical portion 6 and which effects the deformation of the billet 7 once the pressure vessel 3 is pressurised such that the billet is urged through the conical section and out to atmosphere to form the extrudate 8. At the opposite end of the barrel to plug 4 there is positioned plug 9 which contains passageways 10, the passageways constituting an inlet and outlet for the pressure transmitting fluid, castor oil. The extruder is fitted with electric heaters 11.

In the extrusion procedure, it has been found desirable, because of the brittle nature of the chain-extended linear polyethylene resulting from the annealing process, to employ a brass sheath (not shown) to protect and support the billet during the extrusion process. After loading a machined billet with a matching conical section into the hydrostatic extruder, the chamber 3 was filled with castor oil, and the heaters energized. After about one and a half hours the temperature of the fluid within the chamber 3 had reached 100°C. The pressure transmitted by the castor oil was increased to apply a load to the billet to bring about extrusion. This was achieved with a pressure of 52.5 MPa. When a small portion of the extruded 8 emerged from the extruder a hauling-off load was applied in order to keep the extrudate in a linear condition. The pressure was then maintained at that value necessary to ensure a constant haul-off speed for the entire

extrusion procedure. The workpiece (or billet) was extruded through the die at an extrusion speed of up to 20mm/min.; and speeds of about 4mm/min. were usually employed with an imposed deformation ratio of 7. At the termination of the extrusion, the temperature was, in each case, allowed to fall to below 100°C before the pressure was released and the extrudate and the remaining end portion of the billet removed from the extruder.

The billet (before extrusion) had an initial melting point of 142°C and the melting point of the extrudate was 141°C. The Young's modulus of the extruded billet, determined by a three-point bending test at room temperature (10 sec. value) was 30.6 GPa. X-ray studies indicated that the polymer of the extruded billet was oriented.

CLAIMS

1. A process for producing a product comprising linear polyethylene which process comprises forming a workpiece which is to be extruded in the solid phase by consolidating under heat and pressure a mass of solid particulate linear polyethylene, subjecting the resulting workpiece to heat treatment under pressure to cause the polyethylene to crystallise in an extended chain morphology with the melting point of the polyethylene being increased to at least 139.5°C and the density to at least 0.98g/cm^3, and thereafter deforming the workpiece of the resulting polyethylene in the solid phase, for example by passage through a die, to provide the polyethylene product whereby the workpiece is subjected to a deformation ratio of at least 3, and preferably 3 to 25.

2. A process as claimed in claim 1 or claim 2 wherein the linear polyethylene has a weight average molecular weight ($\overline{M}_w$) from 300,000 to 3,000,000.

3. A process as claimed in claim 2 wherein $\overline{M}_w$ is from 350,000 to 1,000,000.

4. A process as claimed in any preceding claim wherein the polyethylene is deformed by extrusion to form a bar, strip, rod or tube.

5. A process as claimed in any preceding claim wherein the linear polyethylene comprises a

filler.

6. A process as claimed in any preceding claim wherein the workpiece is extruded under hydrostatic pressure through a reducing die.

7. A process as claimed in claim 6 wherein the hydrostatic extrusion is draw-assisted hydrostatic extrusion.

8. A process as claimed in any preceding claim wherein the ambient pressure at which the deformation is effected is atmospheric pressure.

9. A process as claimed in any preceding claim wherein the polyethylene is subjected to a deformation ratio of from 4 to 20.

10. A process according to claim 9 wherein the deformation ratio is from 8 to 14.

11. A process for imparting extended chain crystalline morphology to linear polyethylene having a weight average molecular weight of at least 300,000, preferably at least 350,000, which process comprises providing the linear polyethylene as solid particulate material, compacting the material by melting only a surface layer of the particles to form a solid, cohered material which is then subjected to a temperature and pressure at which the linear polyethylene crystallises in an extended chain morphology so that the melting point of the polyethylene is increased to at least 139.5^{o}C and the density is increased to at least 0.98g/cm^3.

12. A process as claimed in claim 11 wherein the compacted polyethylene is heated to a temperature above 220°C while being maintained in the solid phase by applied pressure.

13. A process as claimed in either of claims 11 or 12 wherein the polyethylene is subjected to a pressure of at least 350 MPa during the crystallisation.

14. Oriented linear polyethylene having a weight average molecular weight of at least 350,000, and preferably from 350,000 to 1,00,000 which has been deformed to a deformation ratio of from 3 to 20, and which has a Young's modulus of at least 30 GPa and has a melting point of at least 139.5°C.

15. A process as claimed in claim 1 and substantially as hereinbefore described in the example.

16. Polyethylene when produced by the process claimed in any one of claims 1 to 13 or 15.

17. A set hydraulic cementitious or organic thermoset mass which incorporates as reinforcement polyethylene according to claim 14 or claim 16.

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(54) PRODUCTION OF CROSSLINKED POLYOLEFIN MOLDING

(57) Abstract:

PURPOSE: To obtain a crosslinked polyolefin molding improved in the dispersion of degree of crosslinking in the direction of the thickness by irradiating a crystalline polyolefin with various ultraviolet rays of different wavelengths under specified temperature conditions.

CONSTITUTION: The objective molding is obtained by irradiating a crystalline polyolefin with various ultraviolet rays of different wavelengths under the conditions of a temperature equal to or higher than the crystalline melting point of the crystalline polyolefin. When the crystalline polyolefin is at a temperature equal to or higher than its crystalline melting point, its entire crystalline part is in a molten state, and the transparency is good. Therefore, the markedly improved transmission efficiency of ultraviolet rays increases the crosslinking efficiency. Polyethylenes such as low-density polyethylene, high-density polyethylene, linear polyethylene, ultralow-density polyethylene and ultrahigh-molecular-weight polyethylene are particulalry desirable as the crystalline polyolefins because they can give moldings of high crosslinking efficiency.

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㊹発明の名称　架橋ポリオレフイン成形物の製法

㉑特　願　平2-317459
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明細書

1．発明の名称

架橋ポリオレフィン成形物の製法

2．特許請求の範囲

(1)結晶性ポリオレフィンに、その結晶性ポリオレフィンの結晶融点以上の温度条件で、波長の異なる多種類の紫外線を照射することを特徴とする架橋ポリオレフィン成形物の製法。

(2)結晶性ポリオレフィンと光増感剤からなる成形物に、その結晶性ポリオレフィンの結晶融点以上の温度条件で、波長の異なる多種類の紫外線を照射することを特徴とする架橋ポリオレフィン成形物の製法。

(3)結晶性ポリオレフィンと光増感剤と架橋助剤からなる成形物に、その結晶性ポリオレフィンの結晶融点以上の温度条件で、波長の異なる多種類の紫外線を照射することを特徴とする架橋ポリオレフィン成形物の製法。

(4)請求項(1)ないし(3)のいずれかに記載の架橋ポリオレフィン成形物の製法において、紫外線照射に用いる光源が高圧水銀灯とメタルハライド灯であることを特徴とする架橋ポリオレフィン成形物の製法。

(5)成形物が電線，ケーブルの被覆物である請求項(1)ないし(4)のいずれかに記載の架橋ポリオレフィン成形物の製法。

(6)成形物がチューブ，パイプなどの筒状物である請求項(1)ないし(4)のいずれかに記載の架橋ポリオレフィン成形物の製法。

(7)成形物がフィルム，シートなどの平板状のものである請求項(1)ないし(4)のいずれかに記載の架橋ポリオレフィン成形物の製法。

3．発明の詳細な説明

【産業上の利用分野】

この発明は、紫外線照射架橋法によって架橋ポリオレフィン成形物を製造する方法に関する。

【従来の技術】

ポリエチレンなどに代表されるポリオレフィンの架橋方法としては、電子線などによる放射線架

橋や有機過酸化物による化学架橋などが知られている。

放射線架橋は、架橋効率が良いが、放射線の透過能率の関係で、厚さが1mm程度以下の薄肉の成形品に限られ、また設備費用が高み、操作も危険を伴う欠点がある。

化学架橋は、厚肉の成形品にも適用可能であるが、架橋に時間を要し、また加熱加圧のための架橋設備が必要となる。また、有機過酸化物を添加したポリオレフィン組成物を押出成形、射出成形する際、有機過酸化物の一部が分解し、いわゆるスコーチなどが生成して成形装置の長時間運転に支障を来すことがある。

また、絶縁電線の分野では、シラン架橋法が知られている。このものでは、水との反応によって架橋反応を行わせるため、絶縁層などの被覆の厚さが3～4mm以上となると水の浸透が遅く、架橋に長時間を要する。また、微量の水分が残留し、電気的特性が十分でないなどの不都合がある。

一方、紫外線照射による架橋については、紫外線硬化型塗料やフォトレジストなどの分野で実用化されている。

しかしながら、ポリエチレンなどの結晶性ポリオレフィンに対する紫外線照射による架橋についてはいまだ実用化されていない。

一方、本発明者等は、先に結晶性ポリオレフィンに、その結晶融点以上の温度条件で紫外線を照射することで、結晶性ポリオレフィンを効率よく紫外線架橋できることを知見し、その実用化を進めている。

【発明が解決しようとする課題】

しかしながら、前記方法によって厚肉のものを短時間で架橋させると、紫外線が照射される表面層の架橋は進み易く、厚さ方向に架橋度のバラツキが生じ易いという可能性がある。

【課題を解決するための手段】

本発明は前記課題を解決するためになされたもので、結晶性ポリオレフィンからなる成形物に、その結晶性ポリオレフィンの結晶融点以上の温度条件で、波長の異なる多種類の紫外線を照射したものである。

【作用】

結晶融点以上の温度においては、結晶性ポリオレフィンはその結晶部分が全て融解状態にあり、透明性が良好になる。このため、紫外線の透過効率が大幅に向上し、架橋効率が増加する。

ここで、紫外線照射による架橋効率は、まず被照射体の光の吸収程度により決定される。

一般に光の吸収は次式で表される。

$$A = \varepsilon \cdot d \cdot C$$

A：吸収量（無次元）

ε：光増感剤の分子吸光係数（l／mol・cm）

d：試料厚（cm）

C：開始剤濃度（mol／l）

上式から明らかな通り、試料厚と開始剤濃度を一定とすると、分子吸光係数（ε）が大きい程、吸収量は大きくなる。

この分子吸光係数は物質に固有の値であり、例えば、ベンゾフェノンでは、ε＝18900（λ＝252nm）、ε＝156（λ＝331nm）である。尚、λは、吸収ピークの紫外線波長である。

ところで、紫外線等の光において、波長が長い程、透過性が大きいことはよく知られている。従って、肉厚なものを架橋（重合）させる場合には、長波長側の紫外線を吸収させることが不可欠である。また、紫外線照射架橋（重合）の場合は、空気中の酸素禁止作用が存在し、架橋阻害がある為に、表面付近での架橋（重合）効率を高める必要がある。

本発明では、長波長の紫外線スペクトルを多くもつ光源と短波長の紫外線スペクトルを多くもつ光源を併用することで、前記課題を解決したものである。

以下、この発明を詳しく説明する。

この発明で用いられる結晶性ポリオレフィンとしては、ポリエチレン、ポリプロピレン、ポリブテン－1、ポリ－4－メチルペンテン－1、エチレン・プロピレン共重合体などのエチレン共重合体などがあるが、なかでも低密度ポリエチレン、高密度ポリエチレン、直鎖状ポリエチレン、超低密度ポリエチレン、超高分子量ポリエチレンなど

のポリエチレンが、架橋効率が高いものとなって好ましい。勿論、これらの混合物であってもよい。

この結晶性ポリオレフィンは、光増感剤との混合物として、種々の成形手段によって成形物とされる。この混合物には、さらに架橋助剤あるいはこの架橋助剤と紫外線吸収剤を混合して、成形物とすることもできる。

ここで用いられる光増感剤としては、ベンゾフェノン、4－クロロベンゾフェノン、2－クロロベンゾフェノン、4,4'－ジクロロベンゾフェノン、ヘキサクロロベンゾフェノンなどのベンゾフェノン類や2－ベンジル－2－ジメチルアミノ－1－(4－モルフォリンフェノール)－ブタノンやクロレンディックアンハイドライド、「サンドリー1000」(商品名:モンサント社製)などが用いられる。

この光増感剤の配合量は、結晶性ポリオレフィン100重量部に対して0.2～3重量部程度が好ましく、0.2重量部未満では架橋率向上効果が得られず、また3重量部を越えると過剰となって、架橋後の成形物の電気的特性、機械的特性等が低下して好ましくない。光増感剤の配合により、架橋効率が格段に向上し、短時間で架橋を高いレベルまで持っていくことが可能となる。

また、紫外線吸収剤としては、フェニルサリチレートなどのサリチル酸誘導体、2－(2'－ヒドロキシ－5－メチルフェニル)ベンゾトリアゾールなどのベンゾトリアゾール類、2－ヒドロキシベンゾフェノン、2－ヒドロキシ－4－メトキシベンゾフェノン、2－ヒドロキシ－4－オクトキシベンゾフェノン、2,2'－ジヒドロキシ－4－メトキシフェノンなどのヒドロキシベンゾフェノン類などが好適に用いられる。例えば、フェニルサリチレートは320nm以下の紫外線を吸収するもので最適である。この紫外線吸収剤の配合量は、結晶性ポリオレフィン100重量部に対して0.05～1重量部の範囲で決められる。配合量が0.05重量部未満では紫外線照射時の結晶性ポリオレフィンの劣化を防止する能力が低く、一方1重量部を越えると紫外線劣化を制御することはできるものの照射された紫外線が紫外線吸収剤に吸収される度合が大きくなり、架橋効果が低下し、好ましくない。

また、架橋助剤としては、トリアリルシアヌレート、トリアリルイソシアヌレート、N,N'－m－フェニレンジマレイミドなどの水素受容基を有する化合物が用いられ、結晶性ポリオレフィン分子間の架橋反応に関し、架橋反応を促進するためのものである。この架橋助剤の配合量は結晶性ポリオレフィン100重量部に対して通常0.3～4重量部の範囲が好ましい。0.3重量部未満ではこれらの添加の効果が十分に得られず、4重量部を越えると過剰となり、架橋後の成形物の物性等に悪影響を与えて不都合である。

また、上記光増感剤、紫外線吸収剤および架橋助剤以外に、テトラキス－〔メチレン－3－(3',5'－ジ第3ブチル－4'－ヒドロキシフェニル)プロピオネート〕メタンなどの老化防止剤等の照射時の温度条件下で透明性を損なわない添加剤、充填材を適宜配合することができる。さらに、照射時の温度条件下で発泡する4,4'オキシビスベンゼンスルホニルヒドラジド、アゾジカルボンアミドなどの発泡剤を添加することもでき、これによれば発泡架橋成形物を製造することができる。

また、結晶性ポリオレフィンと光増感剤との混合物あるいは、これに紫外線吸収剤もしくはさらに架橋助剤が添加された混合物の成形手段としては、従来から結晶性ポリオレフィンの成形に用いられている種々のものが適用できる。成形物の形態がシートやフィルムあるいはチューブやパイプなどであれば通常の押出成形機による押出成形が用いられる。また、成形物が電線やケーブルなどの被覆物、例えば絶縁体やシースなどの場合には、クロスヘッドダイを装着した押出機による押出被覆法やテープを巻回する方法などが用いられる。さらに、通常の射出成形法によって成形物としてもよい。ただし、形状が複雑な成形物では、紫外線照射時に結晶融点以上に加熱されるため、その形状が崩れることになるため、適切ではないが、紫外線照射時において、紫外線透過性を有しかつ

耐熱性を有する材料、例えば石英ガラスなどからなる型の内部に成形物を収容するなどの方策を講ずれば、複雑な形状のものであってもよい。また、成形品の肉厚は、形状がシート状のものでその両面から紫外線照射が可能なものでは10～15mmが上限となり、片面からのみの照射では5～8mmが上限となる。勿論、紫外線の強度(エネルギー密度)や照射時間を大きく、長くすれば、さらに肉厚の成形物でもよいが、結晶性ポリオレフィンの紫外線による劣化も同時に進行するので注意が必要である。

次いで、このようにして得られた成形物をその結晶性ポリオレフィンの結晶融点以上の温度条件で紫外線を照射する。

この温度条件は、原則として結晶融点以上とされるが、好ましくはこの結晶融点よりも10～20℃程度高い温度とされる。しかし、あまりに高い温度では結晶性ポリオレフィンの熱劣化が進んで望ましくない。成形物が1種以上の結晶性ポリオレフィンからなるものでは、その温度条件を最も高い結晶融点以上とする。

また、紫外線の照射条件としては、波長が200nm以下でない線源を用いる。

そのためには、高圧水銀灯(波長域250～600nm)やメタルハライド(波長域200～600nm)が適している。

本発明では、相対的に短波長側に紫外線スペクトルを多くもつ高圧水銀灯と長波長側に紫外線スペクトルを多くもつメタルハライドを併用するものである。

また、その強度(エネルギー密度)は、10^{-4}～10^{-6}(アインシュタイン／cm^2・分)の範囲が望ましい。照射時間は、架橋密度、成形品の厚さなどによって変わり、通常は10～60秒程度であるが、この範囲に限られるものでなく、例えば成形品の表面部のみを架橋するものであれば、さらに短時間であってもよい。

さらに、成形物の形状がシートやフィルムなどの平板状のものでは、その両面側に紫外線光源を配すれば肉厚の成形物を短時間に架橋することができる。

また、電線、ケーブルなどの被覆物の場合には、その周囲外方に光源を均一に配して、全外周部分に均一に照射することもできる。また、銅などの金属導体直上に被覆物を設けたものでは、金属導体表面が反射面として紫外線を反射し、紫外線を効率よく利用することができる。また、成形物の形状がチューブやパイプなどの中空の筒状物の場合にはその外周部分から同様にして均一に照射することができ、中空部の内径が大きいときには中空部内に紫外線光源を配置して内外側から同時に照射してもよい。さらに、押出成形機のダイの出口部分に接近して紫外線光源を配置しておき、押出成形直後の結晶融点以上の高温状態で直接紫外線を照射するようにしてもよい。

このような条件での紫外線照射によって、例えばポリエチレンでは約90%までの架橋密度を持つ程度にまで架橋でき、また厚さが3mm程度のポリエチレンのシートでは10～30秒で架橋が行なわれる。

架橋後の成形物は、自然空冷、水冷などの冷却手段によって冷却されて架橋成形物となる。

このような架橋ポリオレフィン成形物の製法においては、結晶性ポリオレフィンが完全に無定形で透明性が良好な状態で紫外線の照射を受けるため、紫外線がよく吸収かつ透過され、成形物の深部にまで到達して均一に架橋が行われる。また、結晶融点以上となっているので、ポリマー分子の動きが活発となっており、架橋反応が一層速やかに進行する。特に、光増感剤を添加することで、その増感作用で光エネルギーの利用効率が向上し、架橋反応が促進され、架橋助剤を添加したものでは活性基の濃度が増加してポリマー分子鎖間の反応を促すことになる。また、紫外線吸収剤の作用により、紫外線による結晶性ポリオレフィン自体の光分解が最小限に抑えられ、若干の架橋率の低下はあるものの光分解に伴う成形物の着色や機械的強度等の低下が防止できる。

以下、具体例を示して作用効果を明確にする。

【実施例】

メルトインデックス（ＭＩ）が１の低密度ポリエチレン１００重量部に対し、光増感剤として４－クロロベンゾフェノンを１重量部、架橋助剤としてトリアリルイソシアヌレート１重量部添加し、断面積１００mm^2の導体上に押出機により１６０℃の温度で絶縁体を厚さ３mmに被覆した。

押出被覆後、絶縁体温度が１５０℃以上に保持されている条件下で紫外線照射した。この際の紫外線照射は、高圧水銀灯（１２０w／cm）を０～１０秒、メタルハライド灯（１２０w／cm）を０～１０秒とした。

紫外線照射後、冷却槽に導き、絶縁電線を得た。

得られた各絶縁電線の内層、中層、外層の各架橋度を調べ、結果を第１表に示した。

以　下　余　白

第　１　表

A	B	架橋度（％）		
（秒）	（秒）	内層	中層	外層
０	０	０	０	０
０	５	７０	３０	１０
０	１０	８５	７０	４０
５	０	１０	４０	８０
５	５	８０	８０	８０
５	１０	８５	８０	８０
１０	０	１０	５０	８５
１０	５	８０	８０	８５
１０	１０	８５	８５	８５

A：高圧水銀灯

B：メタルハライド灯

第１表の結果から、高圧水銀灯とメタルハライド灯からなる紫外線スペクトルの最多波長領域の異なる紫外線を光源に併用することで、内層、中層、外層共に均一な架橋度の絶縁体を得ることができることが認められる。

【発明の効果】

以上説明したように、本発明の架橋ポリオレフィン成形物の製法は、結晶性ポリオレフィンからなる成形物に、その結晶性ポリオレフィンの結晶融点以上の温度条件で、波長の異なる多種類の紫外線を照射するものであるので、肉厚のポリオレフィン成形物に対しても効率よく、その深部まで均一に高い架橋密度で、短時間で架橋させることができる。

出願人　藤倉電線株式会社

(19) JAPANESE PATENT OFFICE

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(22) Date of filing: **27.11.90**

(71) Applicant: **KOMATSU LTD**

(72) Inventor: **SAKASHITA KATSUTOSHI**
NAITO YOSHIHIRO

(54) **ULTRAHIGH-MOLECULAR-WEIGHT POLYETHYLENE COMPOSITION**

(57) Abstract:

PURPOSE: To prepare the title compsn. excellent in mechanical properties, flowability, and moldability by compounding a specific PE and a specific macromonomer in a specified ratio.

CONSTITUTION: 100 pts.wt. ultrahigh-mol.-wt. PE having an average mol.wt. of 1000000 or higher is compounded with 20-100 pts.wt. macromonomer having a group reactive with γ-rays or electron beams attached to at least one molecular end (e.g. a butadiene macromonomer).

⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　平4－198242

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C 08 F 8/00	MJA	8016－4J
110/02		9053－4J
299/00	MRM	7142－4J

審査請求　未請求　請求項の数 1　（全3頁）

㊹発明の名称　超高分子量ポリエチレンの組成物

㉑特　願　平2－321039
㉒出　願　平2(1990)11月27日

⑫発明者　坂下　勝敏　神奈川県平塚市万田1200　株式会社小松製作所研究所内
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明　細　書

1. 発明の名称

超高分子量ポリエチレンの組成物

2. 特許請求の範囲

平均分子量１００万以上の超高分子量ポリエチレン１００重量部と、片末端あるいは両末端にr線または電子線反応性官能基を有するマクロモノマー２０～１００重量部よりなることを特徴とする超高分子量ポリエチレンの組成物。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、超高分子量ポリエチレンの組成物に関するものである。

〔従来の技術〕

超高分子量ポリエチレンは、その分子量が大である故に、溶融時の粘度が極めて高く、そのため、押出し成形については特定の条件下でのみ可能であり、また射出成形は不可能な状態であった。

従って、通常は圧縮成形した単純形状物を機械加工して各種の部品を製作しており、生産性が悪く、高コストであった。

この問題を解決する方法、すなわち、超高分子量ポリエチレンの溶融粘度、流動性を改善し、押出し成形や射出成形を可能とする方法として各種の低分子化合物を添加する方法が提案されている（例えば、特開昭６０－１２４５号、特開昭６２－９６５４７号明細書）。

〔発明が解決しようとする課題〕

従来の技術では、溶融粘度、流動性の改善に主眼がおかれており、確かに低分子化合物を添加することにより、溶融粘度、流動性が改善され、押出しや射出の成形性は向上するが、機械的性質等の物性の低下は避けられなかった。逆に物性を保持しようとすると、低分子化合物の添加量が少量に限定され、成形性はほとんど改善されなかった。

本発明は上記のことにかんがみなされたもので、超高分子量ポリエチレンのもつ機械的性質等の物性を維持しつつ、流動性を付与して成形

容易にした超高分子量ポリエチレンの組成物を提供することを目的とするものである。

〔課題を解決するための手段及び作用〕

上記目的を達成するために、本発明に係る超高分子量ポリエチレンの組成物は、平均分子量100万以上の超高分子量ポリエチレン100重量部と、片末端あるいは両末端にγ線または、電子線反応性官能基を有するマクロモノマー20～100重量部より成る。

この組成物は、低分子量のマクロマーが混合されているため、この状態では、溶融粘度、流動性が改善されており、通常の押出し成形、射出成形が可能である。

次に、押出し成形、射出成形で得られた成形品にγ線または電子線を照射することにより、マクロモノマー、またはマクロモノマーと超高分子量ポリエチレン間に反応を起こさせ、これにより物性の低下を防ぐことが可能となる。このようにして成形性の向上と物性の保持が同時にできる。

本発明で用いられる超高分子量ポリエチレンは、平均分子量が100万以上であれば、いずれの市販品も使用可能である。また添加するマクロモノマーは、熱反応性を有するものは成形中に反応するため好ましくなく、γ線または電子線反応性官能基を有するものに限られる。

この条件を満たすものとしては、スチレン系マクロモノマー、ブタンジエン系マイクロモノマー、アクリル酸エステル系マクロモノマー等がある。そして、この組成物の組成は、マクロモノマーの種類により多少異なるが一般的には、超高分子量ポリエチレン100重量部に対して20～100重量部が望ましい。すなわち、添加するマクロモノマーが20重量部以下では超高分子量ポリエチレンの成形性向上に対する効果が小さく、逆に100重量部以上では超高分子量ポリエチレン本来の物性が損なわれる。

次に、このようにして得られた組成物を用いて成形し、得られた成形品にγ線または電子線を照射してマクロモノマーを反応させる。γ線と電子線の使用は成形品の形状（肉厚）により使いわける。またこの照射によって起こる反応は、(1) マクロモノマーの単独重合、(2) マクロモノマーの超高分子量ポリエチレンへのグラフト化、(3) マクロモノマーによる超高分子量ポリエチレンの架橋の3つが考えられるが、いずれかの場合も照射前に比較して物性の向上が期待できる。

〔実　施　例〕

本発明の実施例を以下に説明する。

分子量100万以上の超高分子量ポリエチレン100重量部と、ブタジエン系マクモノマー100重量部とをV型ミキサーで100℃で攪拌コンパウンドした組成物をサンプルとし、これを高化式フローテスター（200℃、剪断応力5×10^5 dyn ／cm²）を用いて粘度測定を行ない、さらにノズルから押出された糸状物（成形品）及びこれに放射線処理（γ線10kev）を施したものの引張り強度を測定した。

〔比較例－1〕

ブタジエン系マクロモノマーを10重量部ブレンドしたほかは実施例と同じ。

〔比較例－2〕

ブタジエン系マイクロモノマーを低分子量ポリエチレンに置きかえた以外は実施例と同じ。

上記各例の結果を下表に示す。

	添　加　物	溶融粘度(P)	引張強度（kg／cm²）	
			処　理　前	処　理　後
実施例	ブタンジエン系マクロモノマー	4.0×10^5	160	200
比較例1	↑	測　定　不　可	－	－
比較例2	低分子量ポリエチレン	1.0×10^5	130	－
(参考)	な　し	測　定　不　可	220	－

なおこの表において、参考とは、超高分子量ポリエチレン単体である。

上記表に示される結果において、実施例のものは処理後において超高分子量ポリエチレン単体のものとほぼ同等の強度が得られた。また溶融粘度も実施例のものは改善されており、他の

ものはやわらかすぎたり、かたすぎたりして成形不能であった。

〔発明の効果〕

本発明によれば、超高分子量ポリエチレンのもつ機械的性質等の物性を維持しつつ、流動性を付与されて、成形性の向上を図ることができる。

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代理人　弁理士　米原正章

弁理士　浜本　忠

弁理士　佐藤嘉明

(19) JAPANESE PATENT OFFICE

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(21) Application number: **57039943**
(22) Date of filing: **12.03.1982**

(71) Applicant: **NITTO ELECTRIC IND CO LTD**
(72) Inventor: **SEKIGUCHI HIDEO**
JIKOBE ISAMU

(54) **PREPARATION OF SLIDING SHEET**

(57) Abstract:

PURPOSE: To obtain a sliding sheet having improved wear resistance, by heat- treating a sheet obtained by molding powder of an ultrahigh molecular weight polyethylene in such a way that its dimension is not changed, crosslinking it to provide a specific gel fraction.

CONSTITUTION: Powder of an ultra-high-molecular-weight polyethylene (≥ 1,000,000 molecular weight by viscosity method) is fed to a mold, compression molded previously at normal temperature at about 150W300kg/cm^2, the pressure is lowered to about 50W100kg/cm^2, the temperature is raised to ≥ the melting point so that it is melted and molded. The pressure is then raised to about 150W 300kg/cm^2, the polyethylene is annealed to room temperature in this state to give a block, which is processed into a sheet with about 0.05W0.5mm thickness by a lathe, etc., the sheet is heat-treated usually at 90°CW the melting point (preferably 110W125°C) in such a way that its dimension is not changed by fixing it into a frame, etc., and crosslinked by ionizing radiation, etc. to provide 60W90% (preferably 70W80%) gel fraction, so that a sliding sheet is obtained.

⑲ 日本国特許庁（JP）　　⑪ 特許出願公開

⑫ 公開特許公報（A）　　昭58—157830

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7/22		6653—4 F

㊸公開　昭和58年(1983) 9月20日

発明の数　1
審査請求　有

（全　3　頁）

⑤滑りシートの製造法

㉑特　　願　昭57—39943
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㉑出 願 人　日東電気工業株式会社
茨木市下穂積1丁目1番2号

明　細　書

1. 発明の名称

滑りシートの製造法

2. 特許請求の範囲

超高分子量ポリエチレン粉末を加圧条件下で成形して得られるブロック状物を切削してシート状とした後、該シートをその寸法が変化しないようにして熱処理し、次いでゲル分率が60～90％になるように架橋することを特徴とする滑りシートの製造法。

3. 発明の詳細な説明

本発明は滑りシートの製造法に関するものである。

滑りシートは相対運動を行なう部材間に配置され、該部材の運動時にそれらの間に発生する摩擦力を減ずるために用いられている。

従来、滑りシートとして超高分子量ポリエチレン（以下UHPEと称す）を加圧条件下でブロック状に成形し、これを所定厚さに切削したシートが知られている。

このUHPE滑りシートは摩擦係数が低いばかりでなく、耐摩耗性も良好であるという長所を有している反面、高温に曝されると湾曲状に変形し易いという問題がある。

例えば、ケース内壁面とリールに巻回された磁気テープの間にUHPE滑りシートを配置して得られるオーディオカセットを夏期にカーステレオに用いた場合、滑りシートが高温に曝されて次第に湾曲状に変形して磁気テープを過度に圧接するようになり、テープ走行が不安定となり、音質に悪影響が出ることがあった。

本発明者達は従来技術の有する上記問題を解決するため種々検討の結果、UHPE粉末を加圧条件下でブロック状に成形した後所定厚さに切削してシート状とし、次に該シートをその寸法が変化しないようにして熱処理し、その後このシートを架橋せしめゲル分率を所定範囲とすることにより、高温に曝されても湾曲状に変形し難いばかりでなく、摩擦係数が低く且つ耐摩耗性に優れた滑りシートが得られることを見出し、本発明を完成する

に至ったものである。

即ち、本発明に係る滑りシートの製造法は、UHPE粉末を加圧条件下で成形して得られるブロック状物を切削してシート状とした後、該シートをその寸法が変化しないようにして熱処理し、次いでゲル分率が60～90％になるように架橋することを特徴とするものである。

本発明においては、先ずUHPE粉末が加圧条件下でブロック状に成形される。この成形はUHPEの特性から、UHPE粉末を金型に充填せしめ常温で圧力約150～300kg／cm²の条件で圧縮予備成形した後、圧力を約50～100kg／cm²まで下げると共に温度をUHPEの融点以上に上げてUHPE粉末を溶融焼成せしめ、次いで圧力を約150～300kg／cm²まで上げ、この加圧状態を保って室温まで徐冷する方法により行なうことができる。

ここで用いられるUHPEはその分子量が粘度法で約100万以上を示すもので、一般のポリエチレンのそれが約2万～10万であるのに比べ大きなものであり、ハイゼックスミリオン（三井石油化学社製）、ホスタレンGUR（ヘキスト社製）等の商品名で市販されている。

なお、滑りシートに導電性性を付与し、使用時における相手部材との摺動による帯電を防止するため、UHPE粉末にカーボン、グラファイト、金属粉等の導電性粉末を約20重量％程度まで添加して成形することができる。

このようにして得られるブロック状物は、次いで旋盤等により切削され厚さ約0.05～0.5mm程度のシートにされる。このシートはその内部にUHPE粉末をブロック状に成形する際に加えられた応力が未だ残存しており、また切削により表面が微小凹凸状となっているので、本発明においては残存応力の除去および表面平滑化のために熱処理を行なう。

本発明における熱処理はシートを枠に固定して加熱する方法或いはシートを加熱した表面平滑なロールやドラムに沿わせる方法等によりシートの寸法が変化しないようにして行なう。熱処理温度はブロック状物への成形時に加えられる圧力や熱処理時間との兼ね合いによって決定するが、通常90℃～UHPEの融点好ましくは110～125℃である。

上記のようにして熱処理されたUHPEシートは、次いでゲル分率が60～90％好ましくは70～80％になるように架橋される。シートの架橋は例えば電子線、ガンマー線等の電離性放射線の照射によって行なうことができる。この放射線照射法によって、UHPEシートを架橋しゲル分率を上記所定値にするのに要する照射線量は、UHPEの分子量、シート厚さ、照射条件等に応じて決定するが、電子線の場合通常は約10～100メガラッドである。

本発明において、架橋後のUHPEシートのゲル分率が60％以下であると、高温使用時における形状安定性の優れた滑りシートが得られず、ゲル分率が90％以上であるとシートが脆化し機械的強度が低下するばかりでなく、摩擦係数の増大を招くのでいずれも好ましくない。

本発明は上記のように構成されており、UHPE粉末を加圧条件下で成形して得られるブロック状物をシート状に切削し、このシートに対し熱処理および架橋を順次施こすことにより、高温使用時においても形状安定性の優れた滑りシートが得られる特徴がある。

以下、実施例により本発明を更に詳細に説明する。なお、実施例中の部は重量部である。

実施例

UHPE粉末（三井石油化学社製、商品名ハイゼックスミリオン240M）97部に対し、カーボン粉末3部を均一に混合して金型に充填し、温度25℃で200kg／cm²の圧力を10分間加えて圧縮予備成形した後、圧力を50kg／cm²まで下げると共に温度を210℃に上げてこの状態を120分間保ってUHPE粉末を溶融焼成せしめ、次いで圧力を200kg／cm²に上げ、この圧力を保ちながら120分間で室温まで冷却して金型から取り出し、外径80mm、内径40mmの円筒状成形物を得る。

その後、この円筒状成形物を切削し、厚さ100μのシートを得、次いでこのシートの四辺を鋼製枠で固定して寸法が変化しないようにして、120℃の温度で3分間熱処理を行なう。

次に、このシートに対し電子線加速器を用い、空気中で18メガラッドの電子線を照射して架橋せしめ、ゲル分率が66%の滑りシート（試料番号1）を得た。

なお、滑りシートのゲル分率はシートを130℃のキシレン中に24時間浸漬して未架橋部分を溶解せしめた後、架橋された不溶部分を50メッシュのフィルターで3過して取り出して乾燥し、その重量を測定し、下記の式によって算出した値である。

$$\text{ゲル分率(\%)} = \frac{\text{不溶部分の重量}}{\text{滑りシートの重量}} \times 100$$

一方、これとは別に上記の熱処理されたシートを用い、電子線照射量を24メガラッドおよび45メガラッドとする以外は試料番号1の場合と同様に作業し、ゲル分率が73%および80%の2枚の滑りシート（試料番号2および3）を得た。

これら滑りシートの摩擦係数、カール高さおよび引張り強さを下記の試験方法により測定して得た結果を第1表に示す。なお、第1表におけるカール高さの加熱後のデータは滑りシートを100℃の温度で48時間加熱し、25℃の室内に1時間放置した後のデータを示している。

(A) 摩擦係数

バウデン・レーベン型摩擦試験機（東洋ボールドウィン社製、型式EFM－4）を用い、相手材ポリエステルフィルム、摺動速度175㎜／㎜、荷重200g、温度25℃の条件で測定した。

(B) カール高さ

滑りシートを定盤上に置き、ハイトゲージにてその湾曲部の最大高さを測定した。

(C) 引張り強さ

JIS－K－6888に準ずる方法で最大引張り強さを測定した。

なお、比較のため滑りシートを得るために用いた熱処理されたシート（試料番号4）、熱処理シートに対し電子線を5メガラッドおよび150メガラッドとする以外は試料番号1の場合と同様に作業し、ゲル分率が52%および95%になるように架橋して得た滑りシート（試料番号5および6）のデータを同時に示す。

第 1 表

試料番号	ゲル分率(%)	摩擦係数	カール高さ(㎜) 加熱前	カール高さ(㎜) 加熱後	引張り強さ(kg／㎟)
1	66	0.12～0.14	2～4	4～8	2.7
2	73	0.16～0.18	2～3	3～5	2.6
3	80	0.17～0.20	2～3	3～5	2.2
4	0	0.08～0.11	3～4	20<	3.6
5	52	0.10～0.12	2～4	10～15	4.2
6	95	0.25～0.30	1～2	2～3	0.8

上記実施例および比較例から明らかなように、ブロック状物を切削したシートに熱処理および架橋を順次施して得られる本発明品は、高温に曝されても湾曲状態の変化が少ないばかりでなく、摩擦係数が小さく、引張り強さも大きなものであり、実用性が優れていることが判る。

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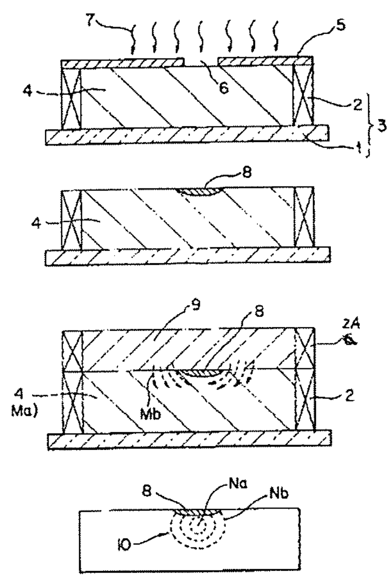
FUNAKI MASAAKI

(54) **MANUFACTURE OF LENS OF REFRACTIVE INDEX DISTRIBUTION TYPE**

(57) Abstract:

PURPOSE: To obtain a refractive index-distribution type lens body for image transmission elements by a method in which a transparent gel substance obtained by partly polymerizing a network-structured polymer-formable monomer is masked by leaving the necessary portion of its surface and a monomer to form polymer having different refractive index is diffused into the gel substance and polymerized by closely contacting the mask and the gel substance.

CONSTITUTION: A monomer (e.g., diethylene glycol bisallyl carbonate) or monomer mixture to form a network-structured polymer (copolymer) is mixed with an initiator and benzophenone, cast into molds 3, and partly polymerized to form a transparent substance 4. A light-shield mask 5 is formed on the surface of the substance 4, an opening 6 matched to the plane pattern of a lens is provided, and light or electron rays are irradiated to the substance 4 to partly harden the irradiated part of the substance 4 to form a mask layer 8. A monomer 9 to form a polymer having different refractive index is then contacted with said polymer and diffused into the gel substance 4 and polymerized to obtain an objective lens of refractive index-distribution type.



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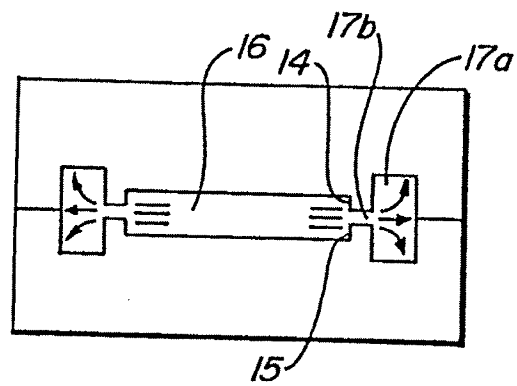

(57) Abstract

A method for producing a UHMWPE product (19) with enhanced planar mechanical properties. An initial UHMWPE semicrystalline morphology is solid-state deformed under compression in a mold (10) comprising a mold cavity (16) with an unenclosed perimeter zone (17) with a reservoir (17a) enabling flow-through (17b) for molded UHMWPE. A polymer preform is oriented and extended in more than one direction in the mold cavity (16) and the perimeter zone (17, 17a). The oriented and extended UHMWPE is cooled under compression to ambient temperature for maintaining the maximum orientation and extension attained during the solid-state deformation process. The UHMWPE product (19) has a markedly transformed morphology, as compared with the initial UHMWPE morphology. The product (19) comprises oriented and extended molecular chains in more than one direction and exhibits markedly enhanced mechanical properties in more than one direction, the magnitude depending on the extent of deformation.

+ See back of page

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"A PROCESS FOR PRODUCING UHMWPE PRODUCT"

SPECIFICATION

Field of the Invention

This invention relates to a novel solid-state-deformation process for producing ultra-high-molecular-weight polyethylene products of both simple and complex shapes, with enhanced mechanical properties. It also relates to the resultant product.

Background of the Invention

The art of controlling the magnitude and the directionality of the physical and mechanical properties of polymers has been a subject of considerable interest to polymer engineers in recent years. Whereas the magnitude has been the basic objective of numerous molecular deformation processes by which the tensile properties can be enhanced significantly, as a result of the chain orientation and extension in some particular direction, usually the machine direction, the directionality has been traditionally addressed by the construction of fiber-reinforced composite structures. In conventional melt-processing, where the objective is the conversion of a polymer raw material into a solid product of some specific shape, the traditional approaches of controlling the thermomechanical history of the polymer melt have not been efficient enough for controlling the properties of the final product. The reason is that some of the chain orientation and extension obtained (produced in the feeding and/or processing zones) has tended to relax through an

uncontrolled molecular relaxation process before the polymer has been completely solidified in the forming and/or shaping stage. The basic objective of obtaining a product of some specified shape has been met, but such a product has had non-isotropic properties.

Homogeneous polymer structures (i.e., structures without fillers or fiber reinforcement) with enhanced mechanical properties in planar directions have been produced recently. This has been done by induced crystallization under curvilinear flow conditions and by solid-state-forming processes. This has resulted in products with multiaxial chain orientation and extension and products with an overall biaxial (but unbalanced) chain orientation and extension. The first approach is more suitable for processing readily melt-processable polymers by rapid output processes, whereas the latter approach can be used also for processing more intractable polymers, such as ultra-high-molecular-weight polyethylene.

For example, a solid-state-forming process of Dow Chemical (known as the SPF Process), is a process for the development of containers with biaxial orientation; the SPF Process comprises the forging of a lubricated polymer preform or a briquette, at a temperature between the softening point and the melt point of the polymer, into a sheet preform, which is automatically clamped and cooled at its periphery and then plug-assist and pressure-formed into a cooled mold to the shape of the finished article (the container). Although the overall orientation of the product is biaxial and results in the substantial enhancement of its mechanical properties, the way it is generated is unbalanced and cannot be controlled to vary topologically in a non-symmetrical fashion (i.e., unlike the deep-draw process).

Similarly, the solid-state-forming process disclosed in U.S. Patent No. 4,747,990 involves the shaping of a polyethylene resin in a closed-mold configuration; the deformation of the polymer (and hence the degree of chain orientation) is non-uniform in different parts of the

product, e.g., of the material close to and against the plunger versus the material against the lower part of the mold cavity.

Both the SPF Process and the process disclosed in Patent No. 4,747,990, as well as other solid-state-forming processes, e.g., the matched mold forging process, operate under "closed mold" conditions. In the SPF Process the outer clamping ring on the periphery of the mold provides a physical constraint to the maximum deformation that one can deform the polymer under compression during the forging step for the fabrication of the sheet preform. Similarly, in the other processes, e.g., the process of U.S. Patent No. 4,747,990, the maximum deformation is controlled by the ratio of the polymer preform dimensions to the mold dimensions.

In addition, many applications may benefit from the development of products with enhanced planar mechanical properties and these require good dimensional stability.

In the case of ultra-high-molecular-weight polyethylene it is very difficult to control this important parameter: first, because this polymer is dimensionally unstable, even during a simple machining operation; second, because when this polymer is oriented, it exhibits a remarkable springback, which also affects the magnitude of the properties of the final product. (Springback refers to the tendency of a formed product to revert partially to its original configuration after removing a compression or tension load, and it is a major concern in solid-state-forming operations.)

Thus, the fabrication of ultra-high-molecular-weight polyethylene products to achieve enhanced mechanical properties and good dimensional stability is a challenging task. Also, it is important to realize that polymer structures with enhanced planar mechanical properties can be used at substantially reduced thicknesses, thus reducing the unnecessary bulk of material that is currently used in many applications for increasing their load-bearing performance. For example, in the case of orthopaedic

prosthetic products, e.g., acetabular liner and tibial plates, their thickness can be reduced without sacrificing their mechanical performance.

An object of this invention is the fabrication of a molded ultra-high-molecular-weight polyethylene product with enhanced and balanced planar mechanical properties and controlled dimensional stability.

Another object of this invention is the fabrication of such an ultra-high-molecular-weight polyethylene product by using an "open mold" configuration.

Another object of this invention is the compression molding of an ultra-high-molecular-weight polyethylene to a deformation ratio which is unrelated to the ratio of the physical dimensions of the polymer preform and the mold cavity and, in contrast, depends only on the material properties of the polymer under the employed processing conditions.

A further object of this invention is the fabrication of wear-bearing ultra-high-molecular-weight polyethylene products of thinner load, having enhanced mechanical properties.

Summary of the Invention

This invention produces ultra-high-molecular-weight polyethylene products with enhanced and balanced planar mechanical properties. It includes the product and a method of making such products for applications benefiting from their enhanced mechanical properties and abrasion performance with enhanced load and/or wear bearing capacity.

Under the scope of this invention, the term "ultra-high-molecular-weight polyethylene" (UHMWPE), means those polyethylenes which have been defined by ASTM as those linear polyethylenes which have a relative viscosity of 2.3 or greater at a solution concentration of 0.05% in decahydronapthalene. This definition applies alike to the description that follows and to the claims.

The nominal weight average molecular weight of the so-defined UHMWPE is several million; it is greater than three million and usually from three to six million; however, other linear polyethylenes of weight-average molecular weight greater than 500,000 and preferably above one million are included within the definition first given.

The present invention provides for the preparation of an UHMWPE product with balanced chain orientation and extension and hence superior mechanical properties. The product is made by compression molding UHMWPE in the form of a preformed solid blank heated at between 80°C and the melting temperature of the polymer used, e.g., approximately 140°C for the as-received powder stock, and preferably between 100°C and 130°C, using a non-enclosed mold design which is heated in the range of 120°C and 180°C, especially between 120°C and 165°C in which the UHMWPE preform can be biaxially deformed under extensional or shear flow conditions. The product is preferably deformed to a deformation ratio which strictly depends on the material properties of the UHMWPE at the processing conditions. The product is simultaneously shaped into the final product.

Because a so-produced UHMWPE has enhanced mechanical properties, the final product can be designed to have a reduced thickness dimension, as compared to UHMWPE produced currently by conventional molding or machining.

The processing methodology of the present invention comprises the solid-state deformation of the UHMWPE preform of a cylindrical or other suitable shape by compressing it between two molding plates (incorporating the actual mold cavity with the practically moldable design or geometrical details) to produce the shape of the final product, and a perimeter access zone for allowing the excess of polymer in the mold cavity to deform past the mold cavity for the purpose of controlling the extent of the deformation of the polymer in the mold cavity. The extent of deformation in the polymer can be determined from the thickness reduction ratio of the polymer preform to its

deformation to the final product, or alternatively by the displacement of fiducial marks on the surface of the preform. The polymer deforms in the solid-state past the mold cavity to the mold plate boundaries or beyond.

By deforming the polymer past the actual mold cavity a) the extent of the molecular chain extension and orientation can be controlled throughout in the final product, an important objective of this invention and b) the excess polymer which deforms past the mold cavity acts as an in-situ-generating tenter frame which can hold the compression deformed polymer in the mold cavity under tension when the compression load is removed after cooling the mold to ambient temperature and hence aid in retaining the attained chain orientation and extension past the compression operation. The so-compression-deformed product in the mold cavity can be maintained attached with the deformed polymer in the perimeter zone for sufficient time after processing until the polymer relaxes in its deformed state or for post-processing such as cross-linking radiation under tension; alternatively; it can be cut off by stamping or other process.

Unlike the conventional compression molding process or the solid-state-forming processes of the prior art, the process of this application requires the employment of high pressure of greater than 20 MPa and preferably above 50 MPa for a) controlling the uniformity of the chain orientation and extension in the product and b) for undercooling the polymer preform when the mold temperature is maintained above the melting temperature of the polymer.

This processing approach is versatile. It makes possible:

1) the fabrication of products with enhanced mechanical properties and having practically any planar shape,

2) the fabrication of products with planar or three-dimensional chain orientation and extension,

3) the fabrication of products with enhanced planar mechanical properties by solid-state deforming to a deformation ratio which depends only on the material properties of the polymer, rather than the physical constraints of the mold cavity,

4) the fabrication of products with mechanical properties which can be designed to be topologically different. This can be accomplished by the use of a polymer preform with larger dimensions and geometrical configuration different from the mold plates.

5) the fabrication of composite products with enhanced planar mechanical properties comprised of the same or different polymer resins,

6) the fabrication of fiber-reinforced composite products comprised of a biaxially solid-state deformed matrix of UHMWPE or other suitable polymer resin and UHMWPE or other suitable reinforcing fibers e.g., aramid (Kevlar), glass, and carbon fibers.

Brief Description of the Drawings

Fig. 1 is a schematic representation in perspective of an opened mold embodying the principles of the present invention. The mold may be circular, rectangular, or of any other shape. A polymer preform is shown between the mold plates.

Fig. 1A is a perspective schematic representation of a mold preform before it is placed between the two mold halves and the mold closed.

Fig. 1B is a perspective view of the molded product removed from the mold.

Fig. 1C is a similar view of the product which results from trimming the perimeter polymer compressed from the product of Fig. 1B.

Fig. 2 is a schematic diagram similar to Fig. 1, of a polymer preform, both outside the mold and between a pair of mold plates (Fig. 2A) as it is being deformed (Fig. 2B and 2C) into a final disc-like product (Fig. 2D), and it shows a plurality of different stages of the process.

Three stages, A, B, and C are shown. The lines in the preform in Figs. 2A, 2B and 2C indicate the direction of the material flow (in the plane of the paper) during the compression process. Three stages, Fig. 2A, Fig. 2B and Fig. 2C are shown. The lines in the preform in Fig. 2A, 2B and 2C indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 3 is a schematic diagram like that of Fig. 2, with a polymer preform (Fig. 3A) comprised of three layers of the same polymer, again at a plurality of different stages of the process (Figs. 3B and 3C). A larger number of layers can be deformed simultaneously in this arrangement. Also, the middle layer(s) can be fiber filled, whereas the outside layers can be unfilled. Again, three stages, A, B, and C are shown, and the final product is shown at Fig. 3D. The lines in the preform in Figs. 3A, 3B and 3C indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 4 is a schematic diagram of a similar mold with an UHMWPE preform between the mold plates (Fig. 4A) as it is being deformed (Figs. 4B, 4C, and 4D) into an acetabular liner (Fig. 4E), and shows it at a plurality of different stages of the process. The liner is the preform in Figs. 4A-4E. The lines in the preform 13 indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 5 is a similar diagram of a modification of the schematic view of the mold in Fig. 4, in which one part of the mold cavity can be moved relative to the rest for controlling the deformation in the product topologically. Steps 5A, 5B, 5C and 5D are shown as well as the final product of 5E. The lines are a preform in Figs. 5A-5E. The lines in the preform 13 indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 6 is a similar diagram of a schematic modification of the preform in Fig. 3 which is comprised of two layers of UHMWPE and a layer of woven or knitted

reinforcing fibers is shown as Fig. 6A; and molding stages 6B and 6C are shown as well as the final product of Fig. 6D. The lines in the preform in Figs. 6A-6D indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 7 is a reproduction of a photograph of an acetabular liner as prepared by this invention, which besides its enhanced mechanical properties, is also fairly transparent, as shown by the print beneath. A product produced by conventional molding or machining is opaque.

Fig. 8 is a schematic diagram of a mold with an UHMWPE preform between the mold plates as Fig. 8A and at a stage (Fig. 8B as it is being deformed into a tibial plate; and as a final product Fig. 8C). The lines in the preform in Figs. 8A, 8B and 8C indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 9 is a reproduction of a photograph of a tibial plate as prepared by this invention. Again the product of this invention besides its enhanced properties, is fairly transparent (as shown by the print beneath), in contrast to the conventionally produced product.

Fig. 10 is a graph, showing tensile stress, versus % elongation behavior of an UHMWPE prepared by (a) this invention and (b) conventional compression molding.

Fig. 11 is a view similar to Fig. 1 in which the perimeter zone is in the form of a reservoir.

Description of Some Preferred Embodiments

According to the invention, solid-state deformed products with enhanced and balanced mechanical properties can be made with high-molecular-weight polymers such as ultra-high-molecular-weight polyethylene by: first, preparing the UHMWPE preform and, subsequently, processing it, using an open-mold configuration 10 of Fig. 1.

There is an upper mold plate 11, a lower mold plate 12, and a polymer preform 13. The UHMWPE can be obtained from ram-extruded or compression-molded stock.

U.S. Patent No. 4,587,163 discloses that the use of a high temperature, i.e., above 220°C, results in a homogeneous melt-crystallized morphology in comparison with a melt-crystallized morphology prepared below 220°C. A UHMWPE preform 13 prepared at above 220°C under, e.g., a pressure of 15,000 psi has better mechanical properties and, upon its solid-state deformation using the methodology of this invention, exhibits better optical properties than a preform prepared at less than 220°C and therefore not having the complete fusion of the UHMWPE.

The processing methodology of this invention comprises the following two steps: a) the thermal condition of the preform and b) its solid-state deformation.

The UHMWPE preform 13 can be heated, prior to its use for the deformation step, outside the mold or in the mold to 80-130°C and preferably between 120°C and 130°C.

The mold in Fig. 1 comprising the mold cavity 16 and the perimeter zone 17 can be heated to a temperature range of 100-180°C and preferably between 120°C and 165°C. The particular mold temperature setting may not coincide with the temperature of the preform prior to its deformation. A suitable choice of temperatures can be made in consideration of the deformation cycle, which can be as short as several minutes and the compression-load conditions.

After heating the polymer preform 13 and the mold 10 to some particular temperatures, the polymer preform 13 is compressed between the mold plates 11 and 12 in Fig. 2A so that it is deformed in the solid state between the plates 11 and 12 to or beyond the mold boundaries 14 and 15 in Fig. 2B to form a perimeter polymer mass 18 in Fig. 2B. The deformation takes place under a gradually increasing compression until the maximum pressure is reached. After the maximum pressure is reached, the mold 10 in Fig. 2 is cooled to ambient temperature; the cooling time can be as short as a few minutes, if rapid cooling is preferred. After cooling to ambient temperature, the product shown in

Fig. 2D comprising the final shaped product 19 with the enhanced properties and the perimeter polymer mass 18 is removed. The final product 19 in Fig. 2D can be separated from the perimeter mass 18 by stamping or other process after its removal from the mold 10, or after thermal (annealing) or post-processing conditions, e.g., radiation cross-linking.

Unlike the prior-art solid-state-forming processes, which involve the solid-state deformation of the polymer to an extent (deformation ratio) which is determined by the relative dimensions of the preform and the mold cavity, in the process of the invention the deformation ratio is controlled by the material properties of the polymer under the employed temperature and pressure conditions during the deformation process. A balance of the deformation ratio in different directions can be attained by adjusting the shape of the preform relative to the shape of the mold cavity, by adjusting the gap and the shape of the perimeter zone in different locations and by moving selected components of the mold cavity (Fig. 5).

Fig. 2 shows the deformation of the preform 13 during its compression into the final product 19. The shaded portion in Fig. 2D shows the removed perimeter polymer 18. At Fig. 2A the mold 10 with its upper plate 11 and its lower plate 12 are shown, along with polymer preform 13. The lines in the deforming preform 13 indicate the direction of the material flow (in the plane of the paper) during the compression process.

Fig. 2 shows the polymer preform 13 at different stages of its deformation under compression in the mold. The preform in the mold at the beginning of the deformation is shown in Fig. 2A, at an intermediate stage in 2B and at the end of the deformation in 2C. The final product 19 is shown at 2D. The shaded portion in 2D shows the removed perimeter polymer component 18. In Fig. 2 at A the polymer preform 13 is placed in the mold 10 and the mold 10 is still under no compression. At 2B the plates 11 and 12 are compressed towards each other, compressing the polymer

preform 13 and resulting in its deformation. The deformed preform is comprised of a portion 19 in the mold cavity 16 and a perimeter polymer component 18 which accumulates in the perimeter zone 17 of the mold beyond the mold boundaries 14 and 15. At 2C there is further compression, and where the so produced polymer configuration is removed from the mold 10 after its cooling to ambient temperature and is separated from its perimeter polymer component 18, it becomes the final product 19 shown in 2D.

Fig. 3 shows the polymer preform 13 comprised of three layers 13A, 13B, and 13C of the same UHMWPE resin at different stages of its deformation. Under compression in the mold, the preform 13 in the mold 10 at the beginning of the deformation is shown in 3A, at an intermediate stage in 3B, and at the end of the deformation in 3C. The final three-layer product 19A is shown in 3D; the shaded portion in D shows the removed perimeter polymer component 18A.

In Fig. 3A the polymer preform 13 comprised of the three layers 13A, 13B and 13C of UHMWPE is placed in the mold 10, and the mold 10 is still under no compression. At Fig. 3B, the plates 11 and 12 are compressed toward each other as described above, compressing the polymer preform 13 and resulting in its deformation. At 3C there is further compression, as explained above and in the examples, to give a polymer configuration comprised of a laminate product 19A in the mold cavity 16 and a perimeter polymer component 18A in the perimeter zone 17 of the mold which, when removed from the mold 10 after its cooling to ambient temperature and separation from its perimeter polymer component 18A, it becomes a final product 19A shown in 3D.

Fig. 4 shows the deformation of ultra-high-molecular-weight polyethylene preform 13 into an acetabular liner or a product 19 that at least looks like an acetabular liner. Again, the sheet-like portion in 4D shows the removed perimeter polymer 28.

In Fig. 4A an open mold 20 with an upper mold member 21 and a lower mold member 22 is shown with a

polymer preform 13 between them. The dotted lines indicate the boundaries of the mold cavity 26 from the perimeter zone 27. At 4B the upper plate 21 compresses the preform 13, so that part of it flows down into a cavity 26 at Fig. 4B within the lower member 22. At 4C the compression continues and at 4D a product comprised of portions 29 and 28 is shown which when is removed from the mold 10 after its cooling to ambient temperature and separated from its perimeter component 28, it results in the final acetabular liner 29 in Fig. 4E.

Fig. 5 shows the deformation of ultra-high-molecular-weight polyethylene preform 13 into an acetabular liner 39 or a product that at least looks like an acetabular liner under conditions which involve the particular displacement of a plunger member 30 (see 5A, 5B and 5C) of a top plate 31 to accomplish the compression deformation of the preform first in a mold cavity 36 of a lower plate 32 and then the displacement of the top plate member 31 to accomplish the compression deformation of a the perimeter polymer 38. The so-produced product comprised of portion 39 and 38 shown in 5D, when removed from the mold after its cooling to ambient temperature and separated from the component (38), it results in the final product 39 shown in 5E.

Fig. 6 shows the polymer preform 43 comprised of three layers 43A, 43B, and 43C of the same UHMWPE resin at different stages of its deformation under compression in the mold. The two outside layers 43A and 43C of the layered polymer preform are of semicrystallized UHMWPE and the middle layer 43B of woven or knitted UHMWPE high modulus and strength fibers. The preform 43 in the mold at the beginning of the deformation is shown in 6A, at an intermediate stage in 6B and at the end of the deformation in 6C. The final fiber reinforced laminate product 49 of UHMWPE with UHMWPE fibers is shown in 6D.

In Fig. 6A the polymer preform 43 is placed in the mold and the mold is still under no compression. At 6B the plates 11 and 12 are compressed toward each other as

described above, compressing the polymer composite preform and resulting in its deformation. At 6C there is further deformation as explained above to give a polymer configuration comprised of a laminate component 49 in the mold cavity and a perimeter polymer component 48 in the perimeter zone of the mold which when removed from the mold after its cooling to ambient temperature and separation from its perimeter polymer component 48, it becomes a final fiber reinforced laminate product 49 shown in 6D. During the compression steps from 6A to 6C, the reinforcing fiber layer 43B is kept under tension.

Fig. 7 is a photograph of an acetabular liner 50 as prepared by this invention, which, besides its enhanced mechanical properties, is also fairly transparent. In comparison, a product produced by conventional molding or machining is opaque.

Fig. 8 shows a schematic diagram of a mold 60 with an UHMWPE preform 63 of 8A as is being deformed in 8B into a tibial-like plate product 69 between mold plates 61 and 62. After separating the plate product 69 from its perimeter polymer 68, it becomes the tibial plate 69 shown in 8C.

Fig. 9 is a photograph of a tibial plate 69 as prepared by this invention. Again, the product 69 of this invention is transparent in comparison to the conventionally produced products.

Fig. 10 is a graph that shows the stress versus & elongation behavior of an UHMWPE prepared by (a) this invention and (b) conventional compression molding.

Fig. 11 is a schematic view of a modified form of mold having a reservoir separated from the mold cavity by a flow-through region.

Example 1

In one experiment, an UHMWPE cylindrical preform 13 (diameter 3 inches) prepared according to the methodology of U.S. Patent No. 4,587,163, by heating a powder stock (Hostalen 412 GUR, weight average molecular

weight greater than 3 million) to 300°C and then cooling to 140-150°C and compressing it under 15,000 psi and then cooling it further to ambient temperature, was heated by air convection in an oven to 90°C (the temperature was measured by a thermocouple inside a reference preform of the same dimensions), and was placed in the mold 10 of Fig. 2 which was preheated to 130°C. Then, the preform 13 was compressed under a pressure of 100 MPa into a disc-like product of deformation ratio approximately 3, as determined from the displacement of marks, in the mold cavity 16 and a perimeter polymer 18 in the perimeter zone 17 as shown in Fig. 2B and 2C. After the maximum pressure is reached, the mold is cooled to ambient, and the final product 19 with the attached perimeter polymer mass 18 is removed from the mold 10 and separated from the polymer mass 18 by machining. Upon removal from the mold and separation from the perimeter polymer mass, the product 19 "shrinks" by springback by only ~8%. The product (3 mm thick) is transparent and free from unfused powder particles and has a Young's modulus of 1.3 GPa and a tensile strength of 126 MPa at 42% elongation.

Example 2

In another independent experiment, an UHMWPE cylindrical preform 13 (diameter 3 inches) prepared from conventionally compression molded stock of the same UHMWPE resin as with Example 1, was heated to 90°C and was placed in the mold 10 (Fig. 2) preheated to 130°C and compressed into a disc-like product 19 of deformation ratio approximately 3 under a pressure of 100 MPa. After cooling the mold 10 to ambient temperature, the product 19 with the attached perimeter polymer mass 18 was removed from the mold and separated from the polymer mass by stamping. Upon removal from the mold 10 and separation from the perimeter polymer mass 18, the product 19 "shrunk" by ~10%. The product 19 (3 mm thick) was transparent but with unfused powder particles dispersed throughout the product; its Young's modulus was 1 GPa, and its tensile strength 91.5

MPa at 104% elongation.

Example 3

The same procedure as with Example 1 was used, with the modification that the final product 19 was separated from the perimeter polymer mass 18 three days after being processed. The product shrank by 1.6%.

Example 4

The same procedure as with Example 2 was used, with the modification that the preform 13 was heated to 80°C, the mold temperature was 128°C, and the compression was 75 MPa. The product 19, after its removal from the perimeter polymer mass 18, shrank by 3%; its deformation ratio was 2, its Young's modulus was 0.8 GPa, and its tensile strength was 81 MPa at 90% elongation.

Example 5

The same procedure as with Example 1 was used, with the modification that a UHMWPE preform portion 13A (a Hostalen 412 GUR) was ""sandwiched" between two thin layers 13B and 13C (2 mm thick) of UHMWPE of the same polymer resin before it was placed in the mold 10 in Fig. 3. The preform components were heated to 95°C, the mold temperature was 130°C and the compression was 200 MPa. The final product laminar 19A in Fig. 3D was transparent. An evaluation of the mechanical properties of one of the deformed thin layers (13B or 13C in Fig. 3C) after its separation from the final product 19A in Fig. 3D showed that the Young's modulus was 1.2 GPa and the tensile strength 92 MPa at 58% elongation.

Example 6

In another independent experiment, an UHMWPE preform 13 (Hostalen 412 GUR) prepared according to the methodology of U.S. Patent 4,587,163, and described in Example 1, was heated to 100°C and after it was placed in the mold 20 (Fig. 4) which was preheated to 155°C was

compressed under 275 MPa into an acetabular shell or liner product 29 in 4D, which was separated from its perimeter polymer mass 28 after cooling the mold 20 to ambient temperature. The acetabular shell or liner 29 in 4E shrunk by approximately 1.5%. The deformation ratio of the hemispherical section of the acetabular product 29 in the mold cavity 26 was uniform and was determined from the displacement of marks on its outer surface to be 2.3. As shown in Fig. 7, the product 50 was fairly transparent. Tensile specimens prepared from ribbons cut along the perimeter of the hemispherical portion of the product 29 exhibited a tensile strength of 60 MPa at a 72% elongation.

Example 7

In another independent experiment, an UHMWPE preform 13 prepared from commercially available compression molded stock (Hostalen GUR 412) was heated to 100°C, and it was placed in the mold 20 shown in Fig. 4, which was preheated to 155°C; then it was processed under conventional compression molding conditions under 10 MPa i.e., in a closed mold configuration, into an acetabular cup product 29. This product, when retrieved from the mold, had shrunk by 12% and was opaque. Tensile specimens prepared from ribbons cut along the perimeter of the hemispherical portion of this acetabular product exhibited a tensile strength of 35 MPa at a 318% elongation. According to prior literature the maximum tensile strength of compression molded UHMWPE is about 40 MPa.

Example 8

In another independent experiment, one layer 43B in Fig. 6 of woven UHMWPE high modulus fibers (Allied Spectra fibers) held under tension 21 was placed between two layers 43A and 43C of UHMWPE (Hostalen 412 GUR) (each 10 mm thick), which were preheated to 120°C; this assembly was used as a preform which was placed in the mold shown in Fig. 6, which was preheated to 130°C and compressed under 120 MPa to produce an UHMWPE laminar product 49, which was

separated from its perimeter polymer mass 48 after cooling the mold 10 to ambient temperature. The so-produced product 49 in 6D was comprised of a solid-state deformed matrix of UHMWPE (two layers) 43A and 43C reinforced with UHMWPE fibers 13C.

Example 9

The same procedure as with Example 8 was used, with the modification that the preform 43 in Fig. 6 was placed in the mold 20 shown in Fig. 4 to produce an UHMWPE laminar acetabular shell or liner 29 comprised of two solid-state deformed layers of UHMWPE reinforced with a layer of UHMWPE fibers in between.

Example 10

In another independent experiment, an UHMWPE (Hostalen 412 GUR) square preform (1.5 in. x 1.5 in.), which was prepared according to the methodology of the U.S. Patent 4,587,163 discussed in Example 1, was heated to 100°C and was placed in the mold 60 shown in Fig. 8, which was preheated to 130°C and was compressed into a tibial-plate-like product 69 shown in 8B under a pressure of 140 MPa. After the mold 60 was cooled to ambient temperature, the product 69 was removed from the mold, and the tibial plate 69 was separated from its perimeter polymer mass 68 shown in Fig. 8C. The so-produced tibial plate 69 was transparent, in contrast to the currently produced products which are opaque. A photograph is shown in Fig. 9. Because of the geometrical complexity of the tibial plate 69 (e.g., its thickness varied from approximately .25 in to .6 in. in different parts of the plate), the evaluation of its mechanical properties was made with tensile samples which were cut off and machined from its back plate side, which was flat. The Young's modulus was 1.2 GPa, and the tensile strength was 87 MPa at 97.5% elongation.

Example 11

The same procedure was used as with Example 10, with the provision that the mold pressure was 250 MPa. The thickness variation range of the tibial plate was reduced to approximately 0.12 - 0.47 in. The Young's modulus was 1.2 GPa, and the tensile strength was 90.7 MPa at 103% elongation. In other words, the thickness of the tibial plate could be reduced without sacrificing its mechanical properties.

In addition to the biomedical uses suggested in this patent application, there are numerous other applications which include impact resistant structures, ballistic applications, structural components combining wear resistance and improved creep, fatigue, and in general load bearing capacity. These points become apparent when one considered the stress -% elongation behavior of an UHMWPE with isotropic mechanical properties as produced by this patent and the conventionally molded UHMWPE in Fig. 10.

The UHMWPE of this application shows a small elastic hysterisis (i.e. the energy dissipated as heat in one cycle of dynamic test), has a significantly higher deformation energy (i.e. energy to deform the material by a specified amount e.g., to a 10% strain at which the conventionally produced UHMWPE deforms plastically), it has a much higher bearing strength (i.e. the maximum usable stress that can be developed by the material at a particular strain) and a significantly higher bulk modulus of elasticity (which relates proportionally to the Young's modulus), and it has a higher resistance to cold flow and hence to creep; preliminary results show also that it has an impact resistance at least 2x higher from the conventionally molded UHMWPE.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. Such embodiments may include

the solid-state deformation of the UHMWPE in a mold in which the perimeter zone is in the form of a reservoir instead of an "open" space around the mold cavity. This is shown in the schematic view of Fig. 11, depicting the polymer deformed in the mold, in which the perimeter zone 17A is a reservoir separated by a mold cavity 16 by a "flow through" region 17B. The flow through region 17B allows excess polymer in mold cavity 16 to flow beyond the mold boundaries 14 and 15 for the purpose of attaining a particular deformation ratio in the mold cavity 16, and to accumulate into or fill the perimeter zone 17A. The solid-state-deformed product in the mold cavity 16 can be separated from its perimeter components generated in the flow through region 17B and the perimeter zone 17A substantially as described previously. Also, the so-produced solid-state deformed UHMWPE can be used as a precursor for its machining into a final product benefiting from the enhanced properties of the solid state deformed UHMWPE.

What is claimed is:

1. A method for producing an UHMWPE product with enhanced planar mechanical properties comprising:

solid-state deforming an initial UHMWPE semicrystalline morphology under compression in a mold comprising a mold cavity and a perimeter zone including:

orienting a polymer preform and extending it in more than one direction in the mold cavity and the perimeter zone to an extent which is limited by the material properties of the polymer under the employed processing conditions, which include the temperature of the initial UHMWPE semicrystalline morphology, the mold temperature, the compression load and the geometrical configuration of the mold cavity and the perimeter zone,

deforming the excess amount of the polymer past the boundaries of the mold cavity into a perimeter zone surrounding the mold cavity for the purpose of controlling the deformation of the polymer product in the mold cavity,

cooling the oriented and extended UHMWPE under compression to ambient temperature for maintaining the maximum orientation and extension attained during the said solid-state deformation process,

separating the polymer product in the mold cavity from the product in the perimeter zone of the mold cavity,

said solid-state deformation process taking place at a mold temperature and compression conditions to obtain an UHMWPE product having a markedly transformed morphology, as compared with the said initial UHMWPE morphology,

said product comprising oriented and extended molecular chains in more than one direction and exhibiting markedly enhanced mechanical properties in more than one direction, the magnitude depending on the extent of deformation.

2. The method of claim 1 wherein the mold cavity is not enclosed.

3. The method of claim 1 wherein the perimeter zone has a reservoir enabling the UHMWPE to flow into it.

4. The method of claim 1 in which the said solid-state deformation process takes place at a mold

temperature and compression condition to obtain an equibiaxially oriented and extended UHMWPE product with enhanced isotropic properties.

5. The method of claim 1 in which the said solid-state deformation process takes place at a mold temperature and compression condition to obtain a biaxially and extended UHMWPE with balanced properties in more than one direction.

6. The method of claim 1 in which the initial UHMWPE semicrystalline morphology is in the form of a melt crystallized preform.

7. The method of claim 1 in which the initial UHMWPE semicrystalline morphology is in the form of a sintered powder preform.

8. The method of claim 1 in which the excess amount of the deformed polymer past the boundaries of the mold cavity in the perimeter zone surrounding the mold cavity acts as a self generating tenter frame by holding the deformed polymer in the mold cavity under tension after its removal from the mold.

9. The method of claim 1 in which the said solid-state deformation process takes place with the UHMWPE preform heated prior to its deformation in the temperature range of 80-120°C at a mold temperature in the temperature range of 120-180°C and under a compression of at least 20 MPa.

10. The method of claim 1 in which the semicrystalline preform is made of a plurality of UHMWPE laminar layers which can be solid-state deformed simultaneously into one laminar product.

11. The method of claim 10 in which at least one of the UHMWPE layers of the semicrystalline preforms is comprised of reinforcing high modulus fibers.

12. The method of claim 11 in which reinforcing high modulus fiber layers are comprised of uniaxially oriented fibers, each said reinforcing layer being separated by a non-reinforcing layer and with its fibers in a different direction from the fibers in adjacent

reinforcing layers.

13. The method of claim 11 in which the layer of fiber reinforcement is in the form of woven fibers.

14. The method of claim 11 in which the reinforcing fibers are ultra-high-molecular-weight polyethylene.

15. The method of claim 1 in which said UHMWPE product is an orthopaedic prosthetic implant.

16. The method of claim 15 in which the orthopaedic product is an acetabular shell.

17. The method of claim 15 in which the orthopaedic product is an acetabular liner.

18. The method of claim 15 in which the orthopaedic product is a tibial plate.

19. A compression mold for solid-state deforming thermoplastic polymers to obtain products with enhanced mechanical properties in more than one direction comprising:

a mold cavity in which the polymer is shaped and is oriented and extended to an extent which is dependent on the material properties of the polymer under the employed processing conditions,

said cavity having a perimeter zone in which excess polymer mass in the mold cavity can deform past the mold cavity boundaries for flow-through for the purpose of controlling the deformation of the polymer product in the mold cavity.

20. The mold of claim 19 wherein said perimeter zone has an unenclosed perimeter that enables said flow-through.

21. The mold of claim 19 wherein the perimeter zone has a reservoir enabling the polymer to flow into it.

22. The mold of claim 19 having movable components on the mold plates for applying different deformation conditions in different parts of the product.

23. The mold of claim 19 having movable components for separating the polymer product in the mold cavity from the perimeter zone.

24. An orthopaedic prosthetic implant of a solid-state deformed UHMWPE in planar directions under compression to a deformation ratio greater than 1, said solid-state deformed UHMWPE exhibiting enhanced mechanical properties including a tensile strength greater than 44 MPa.

25. The implant of claim 24 shaped as an acetabular liner.

26. The implant of claim 24 shaped as an acetabular shell.

27. An UHMWPE with isotropic enhanced mechanical properties comprising:

a solid-state deformed equibiaxially semicrystalline morphology in planar directions to a deformation ratio of about 1-4.

28. An UHMWPE with balanced mechanical properties comprising;

a solid-state deformed biaxially semicrystalline morphology in planar directions to a deformation ratio of about 1-4.

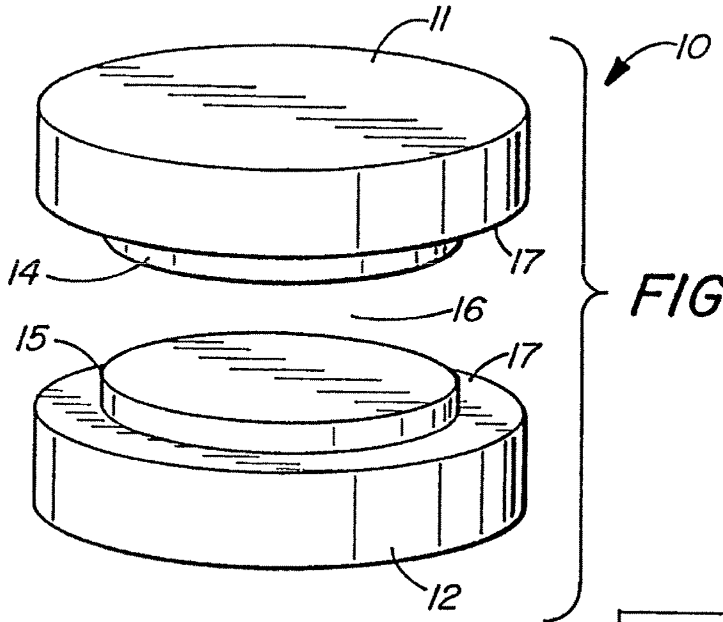


FIG._1.

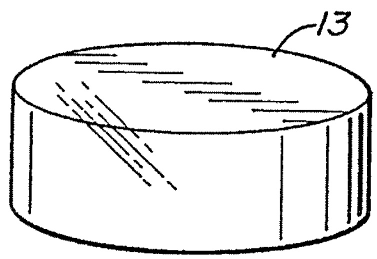


FIG._1A.

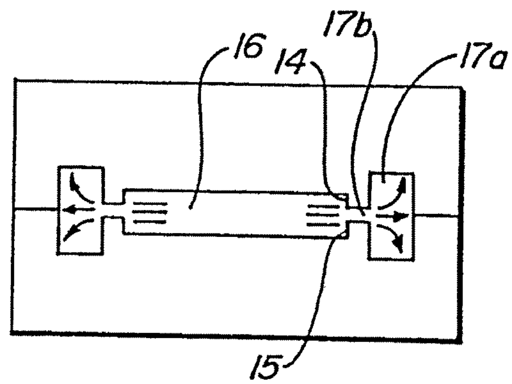
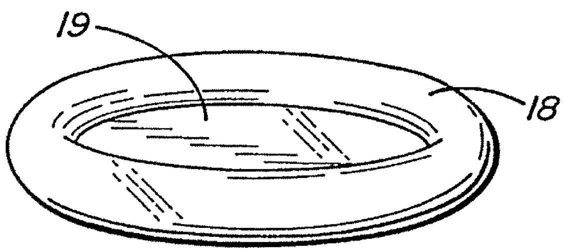


FIG._11.



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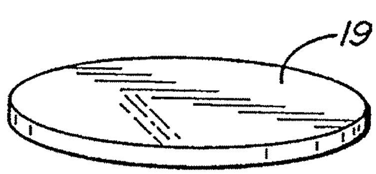

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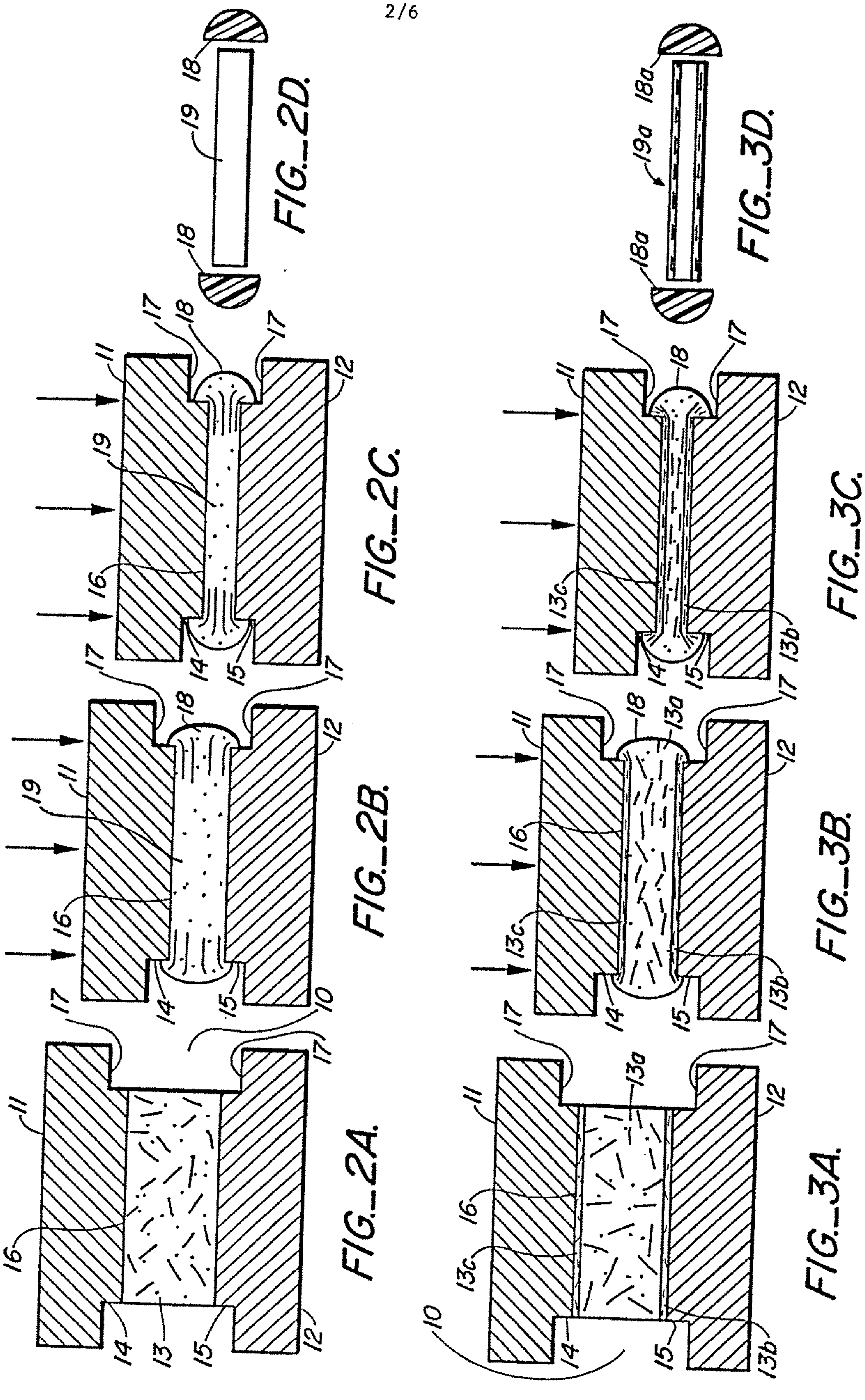

FIG._2A. FIG._2B. FIG._2C. FIG._2D.

FIG._3A. FIG._3B. FIG._3C. FIG._3D.

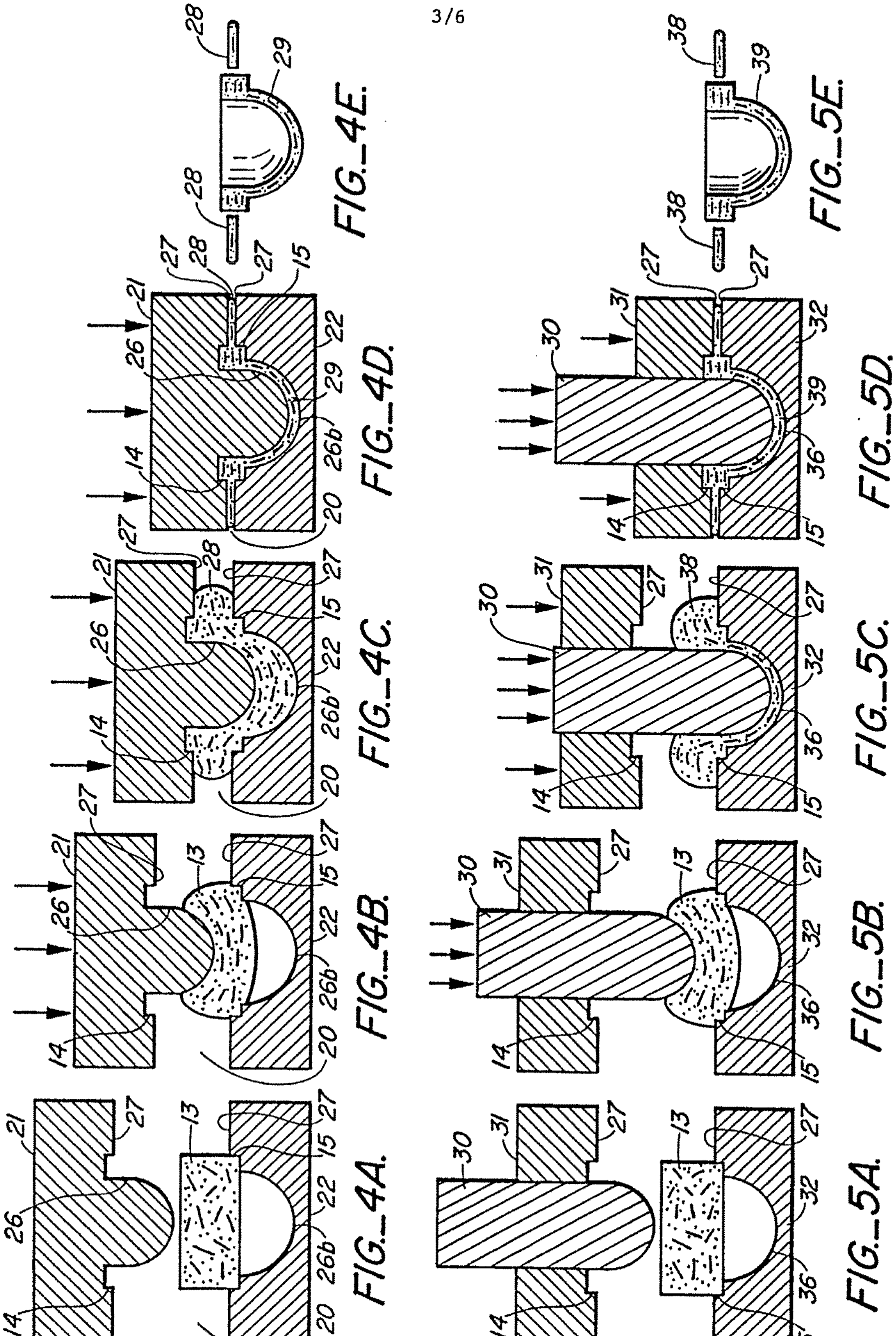

FIG._4A. FIG._4B. FIG._4C. FIG._4D. FIG._4E.

FIG._5A. FIG._5B. FIG._5C. FIG._5D. FIG._5E.

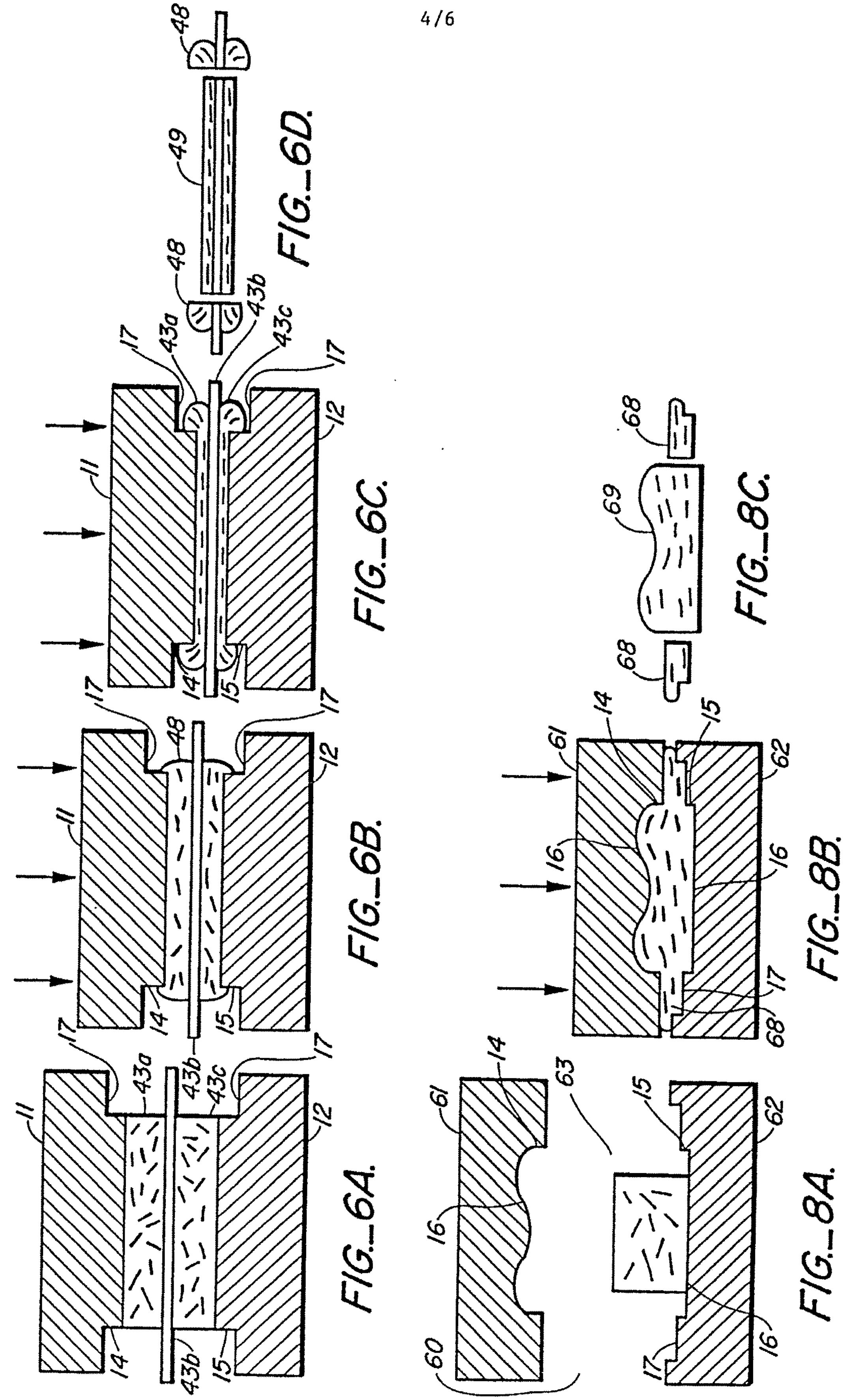

FIG._6A. FIG._6B. FIG._6C. FIG._6D.

FIG._8A. FIG._8B. FIG._8C.

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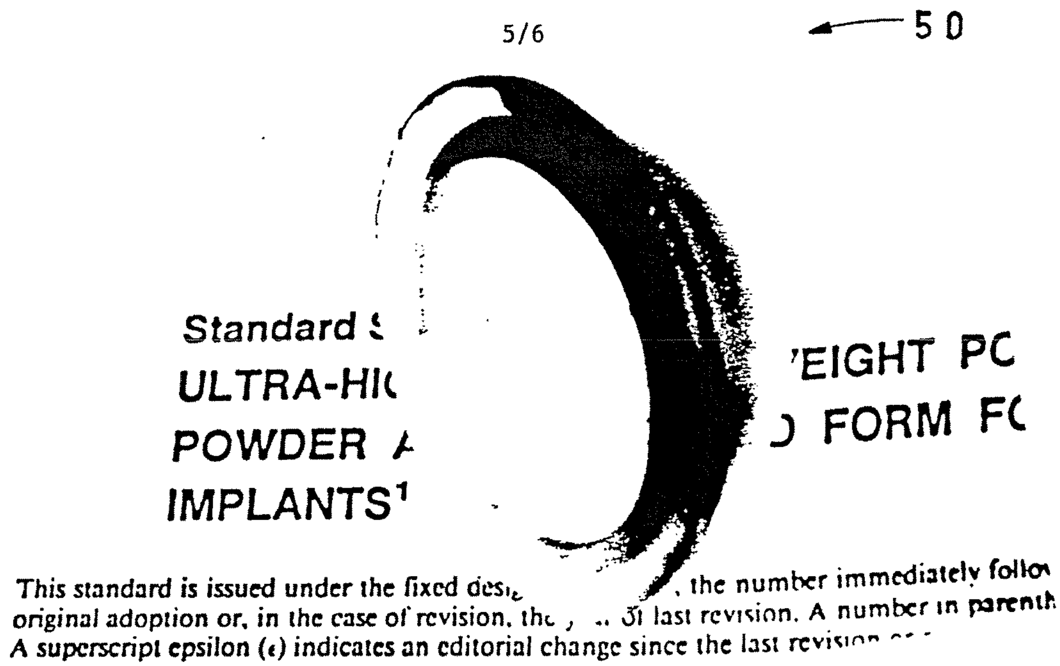
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A superscript epsilon (ε) indicates an editorial change since the last revis

FIG._7.

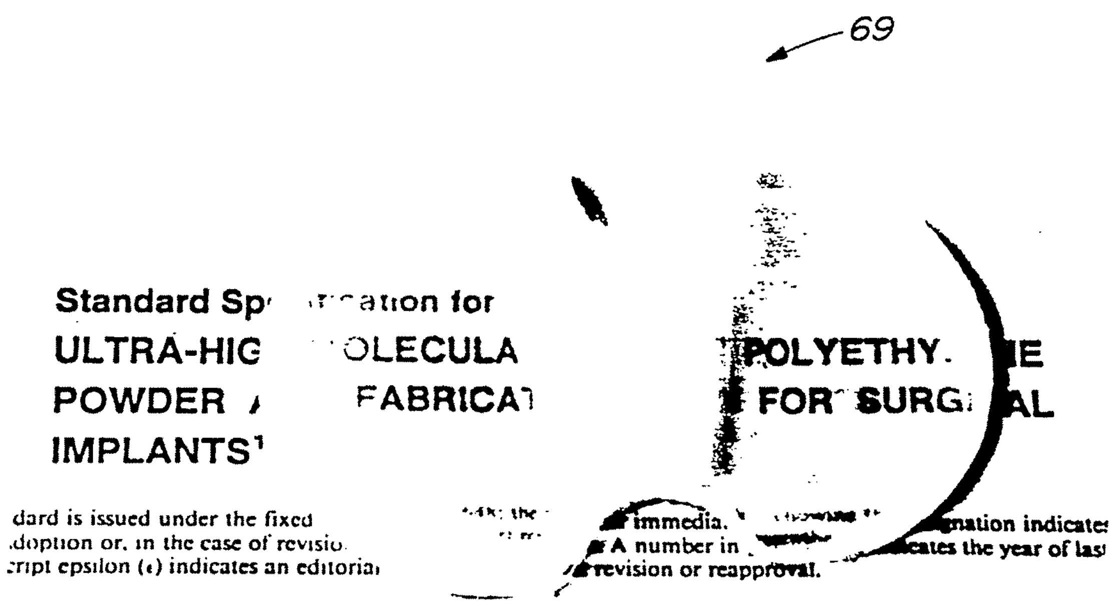
69
Standard Sp
ation for
ULTRA-HIG
OLECULA
POLYETHY
E
POWDER
FABRICA
FOR SURG
AL
IMPLANTS[1]
dard is issued under the fixed
immedia.
nation indicate
doption or, in the case of revisio
A number in
cates the year of las
ript epsilon (ε) indicates an editoria
revision or reapproval.

FIG._9.

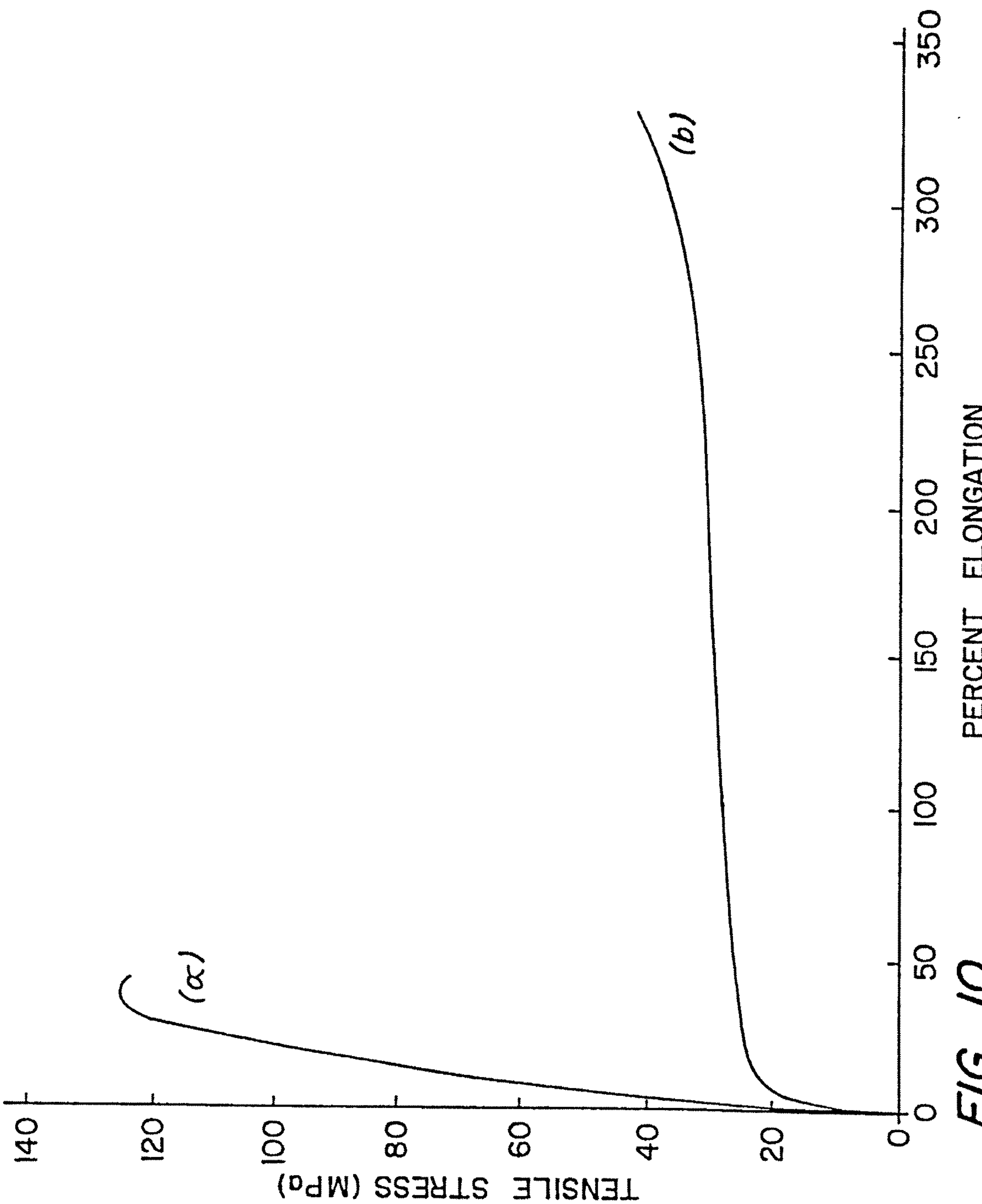
TENSILE STRESS (MPa)
140
120
100
80
60
40
20
0
PERCENT ELONGATION
0
50
100
150
200
250
300
350
(a)
(b)

FIG._10.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/01271

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): A61F 2/02, 2/28, 2/32; B29C 43/16, 43/20; C08F 110/02

US. CL.: 264/322, 323; 425/398, 401; 526/348.1, 352; 623/11, 16, 22

II. FIELDS SEARCHED

Minimum Documentation Searched 4

Classification System	Classification Symbols
US	249/151; 264/322, 323, 331.17; 425/398, 401, 408, 412, 810,812; 526/348.1, 352, 352.2; 623/11, 16,22.

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 5

III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
Y	US, A, 4,014,970, JAHNLE, 29 March 1977. See Figures 1-4; column 2, lines 46-52; column 6, lines 1-6 and 54-58, and column 9, lines 21-31.	1-20
Y	US, A, 3,944,536, LUPTON ET AL, 16 March 1976. See abstract.	1-18, 27, 28
Y,P	US, A, 4,874,657, LO ET AL, 17 Octover 1989 See column 3, lines 4-14 and 28-32; column 4, lines 50-54 and column 6, lines 14-19.	1-7, 9-18, 27, 28
Y	US, A, 4,747,990, GAUSSENS ET AL, 31 May 1988. See column 1, lines 11-16 and 32-34; column 2, lines 45-55; column 3, lines 1-25 and column 7, lines 24-36.	1-18 and 24-28
Y	US, A, 2,976,575, DAUBENBERGER, 28 March 1961. See column 4, lines 62-71 and column 5, lines 20-40.	19-23
Y	US, A, 2,730,766, TOMPKINS, 17 January 1956. See Figures 3 and 4, and column 2, lines 32-47.	19-23
Y	US, A, 3,287,486, JURGELEIT ET AL, 22 November 1966. See column 2, lines 67-70.	19-23

* Special categories of cited documents: 15

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 2	Date of Mailing of this International Search Report 2
06 JUNE 1990	02 AUG 1990
International Searching Authority 1	**Signature of Authorized Officer 10**
ISA/US	Ngoc Ho Nguyen for James B. Lowe NGUYEN NGOC-HO INTERNATIONAL DIVISION

Form PCT/ISA/210 (second sheet) (May 1986)

cdb:7/19/90

International Application No. PCT/US90/01271

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
Y	US, A, 1,909,778, MARSDEN, 16 May 1933. See page 1, lines 53-75.	19-23
Y	US, A, 4,409,169, BARTHOLDSTEN ET AL, 11 October 1983. See column 3, lines 57-68.	19-23
Y	US, A, 4,389,365, KUDRIAVETZ, 21 June 1983. See column 1, lines 52-66.	19-23
Y	US, A, 4,695,243, WATANABE, 22 September 1987. See column 2, line 61 to column 3, line 22.	22, 23
Y	US, A, 4,797,082, HUGHES, 10 January 1989. See column 4, lines 46-60.	22, 23
Y	US, A, 4,587,163, ZACHARIADES, 06 May 1986. See column 4, lines 21-39 and column 5, lines 8-11.	24, 27, 28
Y	GB, A, 2,154,141, BUNING, 04 September 1985. See page 1, lines 71-76.	24, 25
Y	CH, A, 649,913, SCHREIBER ET AL, 28 June 1985. See abstract.	24-26
Y	US, A, 3,847,888, BAUMGAERTNER, 12 November 1974. See column 2, lines 22-35.	27, 28
Y,P	US, A, 4,820,466, ZACHARIADES, 11 April 1989. See column 3, lines 19-38 and column 9, Table 1.	27, 28